DESIGN AND PERFORMANCE OF AN AMMONIA MEASUREMENT SYSTEM

A Thesis

by

CALE NOLAN BORIACK

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2005

Major Subject: Biological and Agricultural Engineering

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Approved by:

Chair of Committee,	Ronald E. Lacey
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ABSTRACT

Design and Performance of an Ammonia

Measurement System. (December 2005)

Cale Nolan Boriack, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Ronald E. Lacey

Ammonia emissions from animal feeding operations (AFOs) have recently come under increased scrutiny. The US Environmental Protection Agency (EPA) has come under increased pressure from special interest groups to regulate ammonia. Regulation of ammonia is very difficult because every facility has different manure management practices. Different management practices lead to different emissions for every facility. Researchers have been tasked by industry to find best management practices to reduce emissions. The task cannot be completed without equipment that can efficiently and accurately compare emissions. To complete this task, a measurement system was developed and performance tested to measure ammonia. Performance tests included uncertainty analysis, system response, and adsorption kinetics.

A measurement system was designed for measurement of gaseous emissions from ground level area sources (GLAS) in order to sample multiple receptors with a single sensor. This multiplexer may be used in both local and remote measurement systems to increase the sampling rate of gaseous emissions. The increased data collection capacity with the multiplexer allows for nearly three times as many samples to be taken in the same amount of time while using the same protocol for sampling.

System response analysis was performed on an ammonia analyzer, a hydrogen sulfide analyzer, and tubing used with flux chamber measurement. System responses were measured and evaluated using transfer functions. The system responses for the analyzers were found to be first order with delay in auto mode. The tubing response was found to be a first order response with delay.

Uncertainty analysis was performed on an ammonia sampling and analyzing system. The system included an analyzer, mass flow controllers, calibration gases, and analog outputs. The standard uncertainty was found to be 443 ppb when measuring a 16 ppm ammonia stream with a 20 ppm span.

A laboratory study dealing with the adsorption kinetics of ammonia on a flux chamber was performed to determine if adsorption onto the chamber walls was significant. The study found that the adsorption would not significantly change the concentration of the output flow 30 minutes after a clean chamber was exposed to ammonia concentrations for concentrations above 2.5 ppm.

I dedicate this thesis to my family and close friends. The support and love that you provide encourages me to strive to do my best every day.

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CHAPTER I

INTRODUCTION: WHY MEASURE AMMONIA FROM ANIMAL FEEDING OPERATIONS

An estimated 70% or more of the total ammonia produced in the United States originates from animal feeding operations (AFOs) (EIIP, 2004). Recently these operations have been under intense scrutiny for their ammonia production. Ammonia is known to have a pungent odor and may cause respiratory diseases in both animals and humans if breathed in large quantities. Particulate matter may form when ammonia reacts with other compounds in the atmosphere further causing respiratory damage. Regulators are under increasing pressure to regulate ammonia emissions. However, ammonia is neither on the list of hazardous air pollutants nor in the national ambient air standard (U.S. EPA, 2004). The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) requires reporting of ammonia emissions greater than 100 lbs per day (U.S. House, 2003). Because emission factors have been developed only for entire operations without regard to management processes, regulators face a dilemma of regulating an emission without an estimate of how much the operation is producing or how a management practice may reduce emissions. Since ammonia production is closely related to management processes, production facilities cannot be regulated just by their animal production status but must be regulated based on facility management practices. A science based emission factor must include relationships to animal type and size, management practices, and climatic effects.

This thesis follows the style and format of *ASAE Transactions.*

Several ammonia emission factors have been published. Most emission factors, however, lack the level of detail needed to use the emission factor for emissions inventory work (Arogo et al., 2003). These factors are often based upon a nitrogen mass balance method. Nitrogen inputs and outputs are calculated to determine the nitrogen loss for a facility. The ammonia production is a function of the nitrogen loss (Phillips et al., 2000). The mass balance method has many limitations that prevent it from being used solely for emission factor determination. These limitations include: the inability to measure the inputs, outputs, and storages accurately; sampling methods and errors associated with them; and only a small portion of nitrogen is emitted as ammonia (Phillips et al., 2000). European studies of emissions factors have generally used the nitrogen mass balance method. Reports by Asman (1992) and Buijsman et al. (1987) indicate that ammonia emissions in Europe for diary cattle are 39.7 kg/animal-year and 12.7 kg/animal-year respectively. The Compilation of Air Pollution Emission Factors-Volume 1 (AP-42) uses an emissions study performed by the National Acid Precipitation Assessment Program in 1980 (U.S. EPA, 1985). The emission factor received a poor rating by EPA for the factor meaning that factor is believed not to be representative of the population. Arogo, et al. (2003) reported that to determine accurate emission factors, measurements of swine emission factors should be taken for different weight, building types, manure treatment systems, and utilization methods.

Currently the only law regarding the emission of ammonia lies in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980. The act provides broad authority to respond to release of hazardous substances that may endanger the public. The act allows the EPA to impose fines on businesses that emit more than the reportable quantity (RQ) of a pollutant and not report the emission. The application of the law to animal feeding operation is questioned since the time of emission is not given and the source is of natural origin. With current emission factors, dairies may have to report emissions if they have as few as 500 head to have an emission of over 100 lb/day of ammonia. Since the act is retroactive, fines could be imposed from the time the act was passed thereby shutting down entire facilities. Currently a handful

of lawsuits over ammonia emissions are being debated in court. Each of the lawsuits cites CERCLA as one reason for suit (US vs. Buckeye Egg Farm, L.P. et al., 2004; CLEAN vs. Premium Standard Farms, 2001).

If lawsuits set precedent for retroactive regulation of ammonia emissions, one can only envision the damage to production agriculture. Assuming the emission factor presented by Asman (1992) was used to determine the threshold for action, the number of head required to meet the threshold would be approximately 418 hd. Currently 58% of Texas dairies hold over 500 head (USDA-NASS, 2002). In the US, 41.9% of the diaries hold over 500 head. Each of these dairies could potentially be affected if retroactive regulation occurs. Science based process emission factors may allow operators and regulators to assess the emission to find a proactive solution.

A proper emission factor must be developed for the livestock facilities to be fairly regulated. Over-regulation causes undo expense to the facility, but under-regulation may be detrimental to public health. Regulators must have the necessary tools to regulate an industry effectively. Regulators may require an industry to develop and employ best management practices (BMPs) in order to reduce emissions.

The process of determining BMPs involves measuring individual processes within a facility. By determining process based emission factors, the agricultural industry may choose management processes that reduce their emissions and therefore improve public health. Accurate data comparing each management practice must be presented in a timely manner. In order to obtain data regarding management practices, efficient use of equipment must be employed.

Process based emission factors are determined by measuring emissions of individual management processes. For example, an open-lot dairy may have several management processes such as open lots, milking parlor, solids separation, lagoons, and compost. Along with the emissions, a nitrogen balance must take place to determine the relationship of the management change to the overall emissions not just the specific management process.

CHAPTER II

MEASURING TECHNIQUES OF AMMONIA

Ammonia measurement varies by measurement technique and measurement sensor. Some measurement techniques are better suited for certain types of facilities than others. This chapter discusses the measurement techniques used to measure ammonia from AFOs and measurement sensors used to measure ammonia.

Measurement Techniques

Several measurement techniques are available to measure ammonia including: nitrogen mass balance, plume sampling, flux enclosures, tracer gas, and source sampling.

Nitrogen Mass Balance

The mass balance method is an indirect method. Physical samples of the source are analyzed for their nitrogen content and by extension their emission potential. By tracking the flow of nitrogen throughout the system, the maximum average emission may be calculated. This method is often used as a check to make sure that the measured emission flux is within the range bounded by the mass balance method. The mass balance method may only be used to determine a range of accepted emissions rates due to the uncertainties associated with measurement of inputs and outputs.

Most of the emission factor development in Europe involved nitrogen mass balance techniques. Agricultural scientists used years of nutritional research to determine nitrogen flows in agricultural products. Emissions were determined by comparing the Nitrogen/Phosphorous ratio across each manure management train (Asman, 1992).

A mass balance involves estimating the inputs and outputs of nitrogen to the AFO. Nitrogen may be input in the form of feed and fertilizer. Nitrogen is removed from the AFO through the sale of agricultural products, volatilization, runoff, and

leaching. Only a portion of the total nitrogen volatilized is released as ammonia (Buijsman et al., 1987).

Nitrogen mass balance has been the preferred method by the US EPA to estimate emission factors and emissions inventories. Battye et al. (1994) used emission factors from Asman (1992) to estimate the emissions inventory for agricultural husbandry operations in the United States. Deficiencies in the knowledgebase were noted from the study with regard to applicability of European data to developing emission factors for the United States. Recent updates correlating to measured data may provide a better estimate of emissions from AFOs (US EPA, 2004).

The advantages of this method are that the method is inexpensive, following a "cookbook" style for easy baseline regulations, and it lends itself easily as a check for other methods. The limitations of this method are that it is difficult to characterize all inputs and outputs and it relies on a large number of critical assumptions. This method is likely to be used for regulatory purposes.

Plume Sampling

Plume sampling involves measuring upwind and downwind concentrations and modeling the dispersion of ammonia. The plume sampling method involves sampling upwind and downwind of the source and back calculating the emission rate using dispersion modeling. This method may be used with a tower to determine the shapes of plumes. The sampling method is similar to the particulate sampling methods described by Sweeten et al. (1998). Dispersion modeling may be based upon Lagrangian or Gaussian models to develop an emission rate. The solution of the Lagrangian model in stationary homogeneous turbulence is the Gaussian model (Seinfeld & Pandis, 1998).

Plume sampling is best used for sampling moderate to high emission rates. Low emission rates may disperse such that the concentration falls below the detection limit of the sampler. However, plume sampling involves "chasing the plume." For example, if the wind drastically changes from North to West, and the sampler is set to sample down wind of a North wind, the sampler no longer collects an emission from the source in a

West wind. The dispersion modeling does not take into account every condition. Because it is a model, several simplifications are made that may introduce error if the conditions don't match the model. The field labor requirements of this method are reduced dramatically from the flux enclosures method described later in this chapter. However, the labor requirements are higher in the data processing and analysis stage due to the requirements of modeling to obtain an emission rate from a downwind concentration.

The advantages of the plume sampling method and limitations are presented as follows:

Advantages

- No flush time.
- Surface moisture conditions not a factor
- No change to temperature and relative humidity occur.
- The plume sampling may be used for compounds for which the volatilization is either liquid or gas controlled.
- An unlimited number of sensors may be used to measure gas concentrations.
- Reduced labor in the field.
- May be used for 24-hour sampling periods

Limitations

- Plume sampling measures gas emissions indirectly.
- Wind direction changes result in "chasing the plume."
- Low emission rates may have concentrations below the detectable limit of the sensor.
- Modeling is imperfect.

Flux Enclosures

Flux enclosures are small chambers that are placed over the emitting source. Purified air is introduced at a known rate and the exhaust concentration is measured. The flux of the source is calculated using:

$$J = \frac{QC_{mass}}{60000A_{fe}} \tag{2.1}$$

where:

J =emissions flux [$\mu g/m^2/s$]

Q =flow rate [L/min]

A_{fe} = Area of the footprint of the flux enclosure [m^2]

C_{mass} = Mass concentration [$\mu g/m^3$]

Two basic types of flux enclosures exist: flux chambers and wind tunnels. The airflow is not given a particular direction in the flux chamber. Rather, the sweep air is blown toward the center of the chamber causing eddies to occur. In a wind tunnel, air is blown across the surface with a given direction.

Sampling points are chosen at random for a given manure management train. Keinbusch (1986) gives practical guidance on the sampling protocols for the chamber. The sampling protocol may be adapted to wind tunnels easily.

The flux chamber theory is based on the two-film model (Jiang and Kaye, 1996). The two film model is often referred to as the phenomenon of volatilization of organic compounds. This means that the flux chamber may not be used for gases for which the volatilization process is gas phase controlled. Both hydrogen sulfide and ammonia are liquid phase controlled (information computed from Linstrom & Mallard, 2005 and Jiang & Kaye, 1996). Only quiescent surfaces may be sampled with a flux chamber since the technology is based on the two-film model. The flux chamber cannot be used for turbulent sources.

According to Eklund (1992), the most important operating parameter is the sweep air flow rate. The optimum sweep air flow rate depends on the design and operating conditions of the chamber. If the sweep air flow rate is not operating at optimal conditions, the emission flux may either be underestimated or overestimated. At high concentrations of the gas being sampled, the flux chamber may actually retard the emission of the gas from the GLAS. This occurs because the concentration nears the gas/liquid equilibrium. Because the equilibrium is temperature and humidity dependent, it cannot be easily determined.

The residence time for the chamber is defined as the time to completely fill the chamber one time. Eklund (1992) suggests 3 to 4 residence times of flush before sampling. For example, a 65 L chamber requires approximately 40 minutes of flush at 5 Lpm before sampling can occur. With a single chamber system, this equates to 40 minutes of flush time per sample where the sensors are not being used.

The advantages of the flux chamber method and limitations are presented as follows:

Advantages

- Simple inexpensive method to measure gaseous emissions directly.
- EPA protocol method.

Limitations

- Different styles and sizes of chambers
- The flux chamber may only be used for quiescent surfaces. It cannot be used for turbulent surfaces.
- Temperature and relative humidity are influenced by solar heating during sampling
- The flux chamber requires a 40 minute flush time before sampling.
- The flux chamber may only be used for compounds for which the volatilization process is liquid controlled (both hydrogen sulfide and ammonia are liquid controlled).

- Sweep air flow rate must be matched to the chamber type so that emissions are not overestimated or underestimated.
- Emission rate may be retarded at high concentrations in the chamber.
- Emission rate may be increased due to surface disturbance.
- May only be used during daytime due to worker safety.

Wind tunnels are rectangular structures placed over the GLAS. A fan generates airflow through the rectangular sample chamber in such a way that the airflow sweeps across the surface in a linear motion. The wind velocities range from 0.1 to 1.2 m/s (Schmidt & Bicudo, 2002). This wind speed approximates the ambient wind speed. By duplicating the ambient wind speeds, one may be able to obtain a more accurate sample. The inlet air may be filtered for the compound to be measured. Inlet and outlet concentrations are measured to ascertain that the sampled conditions as close as possible to ambient conditions. If the wind tunnel is set to filter the air, only the outlet sensor is needed for the wind tunnel. In this case, the wind tunnel and flux chamber methods may be compared side-by-side.

Wind tunnel theory is based upon the boundary layer theory (Jiang & Kaye, 1996). Both quiescent and turbulent surfaces may be sampled with a wind tunnel. The time between samples is reduced from the single flux chamber method because of the increased flow rate. The wind tunnel is best used for high concentrations of the gas being sampled. Since the flow rate is much higher for a wind tunnel, more dilution occurs. At low concentrations, the dilution may cause the concentration to be below the detection limit of the sampler. The increased flow rate reduces changes in humidity and temperature within the system. The reduced response time gives the ability to increase the number of sensors which sample the air. Since no standards exist for the design of the technology, different size and shape relationships may affect emissions. To avoid this problem, Schmidt and Bicudo proposed a standard design for a wind tunnel (2002). The proposed design follows a wind tunnel developed by Lockyer (1984).

The advantages of the wind tunnel method and limitations are presented as follows:

Advantages

- The wind tunnel method measures gaseous emissions directly.
- Flush time is significantly less with a wind tunnel due to the increased wind speeds.
- The wind tunnel may be used for quiescent surfaces and turbulent surfaces.
- Temperature and relative humidity are relatively close to the ambient conditions due to the rapid air exchange of the system.
- The wind tunnel may be used for compounds for which the volatilization is either liquid or gas controlled.
- An increased number of sensors may be used to measure gas concentrations.

Limitations

- Air flow rate must be matched to the ambient conditions so that emissions are not overestimated or underestimated.
- Low emission rates may have concentrations below the detectable limit of the sensor.
- Emission rate may be increased due to surface disturbance.
- No standards for technology.
- May only be used during daylight at some sites due to worker safety.

Trace Gas

The trace gas method involves releasing a trace gas at a given rate. The concentrations of ammonia and trace gas are measured downwind. The flux of ammonia may be calculated using equation 2.2.

$$\frac{J_{NH_3}}{J_{tracer}} = \frac{C_{NH_3}}{C_{tracer}} \quad (2.2)$$

where:

J_{NH_3} = Flux of ammonia [$\mu g/m^2/s$]

J_{tracer} = Flux of trace gas [$\mu g/m^2/s$]

C_{NH_3} = Concentration of ammonia [$\mu g/m^3$]

C_{tracer} = Concentration of trace gas [$\mu g/m^3$]

The trace gas method has been used in the Netherlands to measure the ammonia emissions from naturally ventilated buildings (Mosquera et al., 2005). Sulfur hexafluoride (SF_6), the trace gas, was injected near the NH_3 source. The concentrations of both SF_6 and NH_3 were measured near the exhaust of the building. A gas chromatograph fitted with an electron capture detector (ECD) was used to measure the SF_6 concentration and an AMANDA rotating annular denuder was used to measure the concentration of NH_3 (Scholtens et al., 2004).

The advantages of the trace gas method and limitations are presented as follows:

Advantages

- May be used in naturally ventilated and mechanically ventilated structures
- Dispersion modeling not required.

Limitations

- Trace gas must be emitted near ammonia source
- Multiple trace gas outlets required for sampling
- Multiple measurement points required in building

Source Sampling

Source sampling involves measuring the flowrate and concentrations of exhaust points. This method is primarily used for mechanically ventilated structures and industrial exhaust stacks. Heber et al. (2001) developed a methodology to sample swine finishing barns. Dust was filtered at each sampling point with the use of a Teflon membrane filter.

Measurement of airflow is by far the greatest challenge in mechanically ventilated buildings. The airflow from each fan changes with the static pressure of the building. The static pressure changes with the number of fans running and the speed of variable speed fans. Fan performance generally does not match fan curves. The performance of a fan varies with the loading of dust on the blades. One method of measuring fan performance is by using the fan assessment numeration system (FANS) system developed by Simmons et al. (1998). Fans are tested in place with static pressures ranging from free air to 40 Pa (Gates et al., 2004). With the use of FANS a new fan curve may be developed for each fan in approximately 30 minutes.

The advantages of the source sampling method and limitations are presented as follows:

Advantages

- May be used in mechanically ventilated structures
- Dispersion modeling not required.

Limitations

- May not be used in naturally ventilated systems
- Multiple trace gas outlets required for sampling
- Multiple measurement points required in building
- Adsorption on dust not quantified

Measurement Sensors

Ammonia emissions may be in the form of ammonia gas and ammonium particulate. Ammonia emissions may be measured using continuous emission monitors, wet chemistry, and particulate samplers. Ammonia gas is measured by many different methods including chemiluminescence, near-infrared light, ultraviolet (UV) light, electrochemical cells, and wet chemistry.

Ammonia gas measurement

Chemiluminescence involves converting the ammonia to nitric oxide and measuring the luminescence caused by nitric oxide and ozone reacting in the mixing chamber (Thermo, 2002a). The chemiluminescence analyzer measures NO, NO_x, and NH_3. A stainless steel converter heated to 750ºC is used to convert NH_3 to NO. A molybdenum converter heated to 325°C is used to convert NO_2 to NO. The analyzer multiplexes the three sampling streams to determine the concentration of NH_3.

Near -infrared sensors include photo-acoustic and direct optical absorption sensors. Infrared detectors detect light absorption at 1500 nm wavelength range (Webber et al., 2001). This wavelength is chosen to reduce interference of water and carbon dioxide present in the measured gas. The photo acoustic sensor measures pressure differences caused by ammonia absorbing and desorbing light (Bozoki et al., 2002). The direct optical absorption sensor measures the adsorption of a selected ammonia adsorption line (Bozoki et al., 2002).

Ultraviolet instruments based upon differential optical absorption spectroscopy (UV-DOAS) have been used for open path measurement of ammonia from area sources. Ammonia absorbs UV light in the 190-230 nm range (Phillips et al., 2001). A Xenon light source is focused on a receiver placed up to 1000 m away (Myers et al., 2000). A tunable spectrometer measures the absorption of ammonia. The modulated light source emits one wavelength that ammonia does not absorb and one wavelength that ammonia absorbs. The instrument has an interference with components that may attenuate the light beam (Stevens et al., 1993). These components may be fog, rain, high humidity

and dust. Alignment of the transmitter and receiver could be troublesome in field measurements without an auto alignment mechanism.

Electrochemical cells are small semiconductor circuits that are sensitive to certain chemicals. The resistance or capacitance changes with concentration. These sensors have been primarily used as toxic gas monitors. The EC-NH_3-100ppm (Manning Systems Inc, Lexana, KS) has an accuracy of 5% and a repeatability of 2% full scale (Manning, 2002). Wenger et al. (2005) reported that the Toxi-Ultra ammonia sensor (Biosystems Inc., Middleton, CT) performed poorly in an agricultural facility. Hydrogen sulfide reacted with the sensor causing erroneous readings and premature failure of the sensors.

Wet chemistry involves absorbing ammonia onto an acid solution. The The ammonia measurement by annular denuder sampling with on-line analysis (AMANDA) system uses a rotating annular denuder to capture ammonia. Ammonia gas is absorbed in the acid solution that is pumped through the denuder. Sodium hydroxide is added to the acid solution and passes across a membrane to deionized water where the conductivity is measured (Phillips et al., 2001). Classic denuders have used dried oxalic acid or citrus acid. The acid is washed from the sampler and then titrated with sodium hydroxide to determine the concentration of ammonia (Leuning et al., 1985).

Particulate Ammonium

The measurement of particulate matter and ammonia in the past has generally been a disjointed process. This was primarily because of the lack of understanding of the atmospheric phenomenon in the formation of particulate ammonium.

Particulate matter is generally measured using a gravimetric sampler. This sampler has an inlet that excludes certain size particles. Currently total suspended particulate (TSP), PM_{10}, and $PM_{2.5}$ inlet heads are available. A filter placed after the inlet captures particles that penetrate the inlet. A vacuum pump is used to pull air though the inlet head and filter at a measured flow-rate. Gravimetric sampling entails weighing a filter before and after sampling to determine the weight of particulate

collected. The mass of particulate collected on the filter is converted to a concentration using the time and volumetric flow-rate. Filters must be conditioned in a laboratory setting for 24 hours prior to weighing to reduce the errors associated with changes in relative humidity from the field (US EPA, 1998). Since filters must be weighed in a laboratory setting, volatilization of semi-volatile particles can cause errors in sampling. Additionally, the filter will cause a change in the equilibrium between the ammonium particle and the ammonia (Ferm et al., 1988). The change in equilibrium will cause ammonia to off gas from the particulate as the sample is collected.

Since ammonium particulate is in the form of a semi-volatile particle, it cannot be measured by gravimetric means. This is because of the ammonia re-volatilizing from the filter, resulting in an error in the measurement of particulate matter. Without special care, ammonium particulate contribution to the ambient ammonia concentration is not taken into account in the measurements.

Several techniques compared by Ferm et al. (1988) may be used to measure both particulate and gaseous ammonia. One method uses a filter pack for which one filter is impregnated with a sorbent (oxalic acid) and combined with a pre-filter. The pre-filter is used to remove the particulate. This method is useful when measuring the total ammonia concentration (particulate and gas). However, it was shown to overestimate the ammonia gas concentration. This is because of the equilibrium between the gas and particulate phases changes with the pressure drop across the pre-filter. Another method used to measure total ammonia is to use a single filter treated with a sorbent. Only total ammonia is measured with this method.

Denuder techniques have been used to measure the concentrations of ammonia gas and ammonium particulate accurately. Denuders take advantage of the fact that the two phases have different diffusivities in air. The ammonia gas is thus removed from the particulate ammonium as the air passes along a coated surface under laminar flow. The particles are collected on a filter. A second denuder is placed after the filter to catch any ammonia gas that volatilizes off of the filter.

Van Putten and Mennen (1995) compared five different techniques for measuring ammonium aerosol. The five methods included three variations of low volume samplers as well as a filter pack and annular denuder method. The low volume sampler method entails sampling as a flow-rate of 1.8 L/min for 24 hours. A denuder filled with active charcoal was mounted in front of the filter. Several variations of filters were used, including: standard 8-micron pore size ash-less filter, 8-micron pore size filter impregnated with citric acid, and a three filter setup. The three filter setup consisted of three 8-micron pore size filters, with filter one being untreated; filter two treated with sodium fluoride, and the third impregnated with citric acid. This filter pack used was similar to the filter pack used by Ferm et al. (1988) except that citric acid was used instead of oxalic acid. The denuder setup included a 2.5-micron pre-separator, two denuders coated with sodium carbonate, one denuder coated with citric acid, and a filter pack with a Teflon filter and citric acid impregnated filter. Ammonium sulfate aerosols were generated and mixed with ammonia gas. The particle size distribution of the aerosol was determined with a scanning mobility particle sizer (TSI SMPS model 3934). Van Putten and Mennon (1995) found that the low flow samplers in each case reported concentrations lower than the annular denuder. One of the main problems with the measurement techniques using a denuder is the response time. The denuder often requires 8 to 24 hours of ammonia flux before it can be analyzed. This poses a problem when trying to analyze contributions from an area source. Often the wind direction will change significantly throughout the day resulting in capture of gas only part of the time.

CHAPTER III

CHALLENGES FACING AMMONIA MEASUREMENT FROM AGRICULTURAL FEEDING OPERATIONS

Measuring ammonia from AFOs is a difficult and expensive task to perform. Many factors affect ammonia emissions ranging from management decisions to climate conditions. Many challenges exist when measuring ammonia from agricultural feeding operations.

Facilities from animal feeding operations may be classified into two types: barns and open areas. An AFO usually contains multiple facilities throughout its operation. Design of such facilities varies depending on the contractor used. However, guidelines and standards exist for the design and use of specified types of facilities. Guidelines are available from Midwest Plan Services, CIGR, ASHRAE, and ASABE.

Factors Affecting Ammonia Production

Many factors affect ammonia production from animal feeding operations. Understanding how ammonia is emitted and the factors affecting the emissions provides an important strategy for reducing emissions. To understand how ammonia is produced, the processes of waste breakdown must be examined. Figure 3.1 details the breakdown of animal waste.

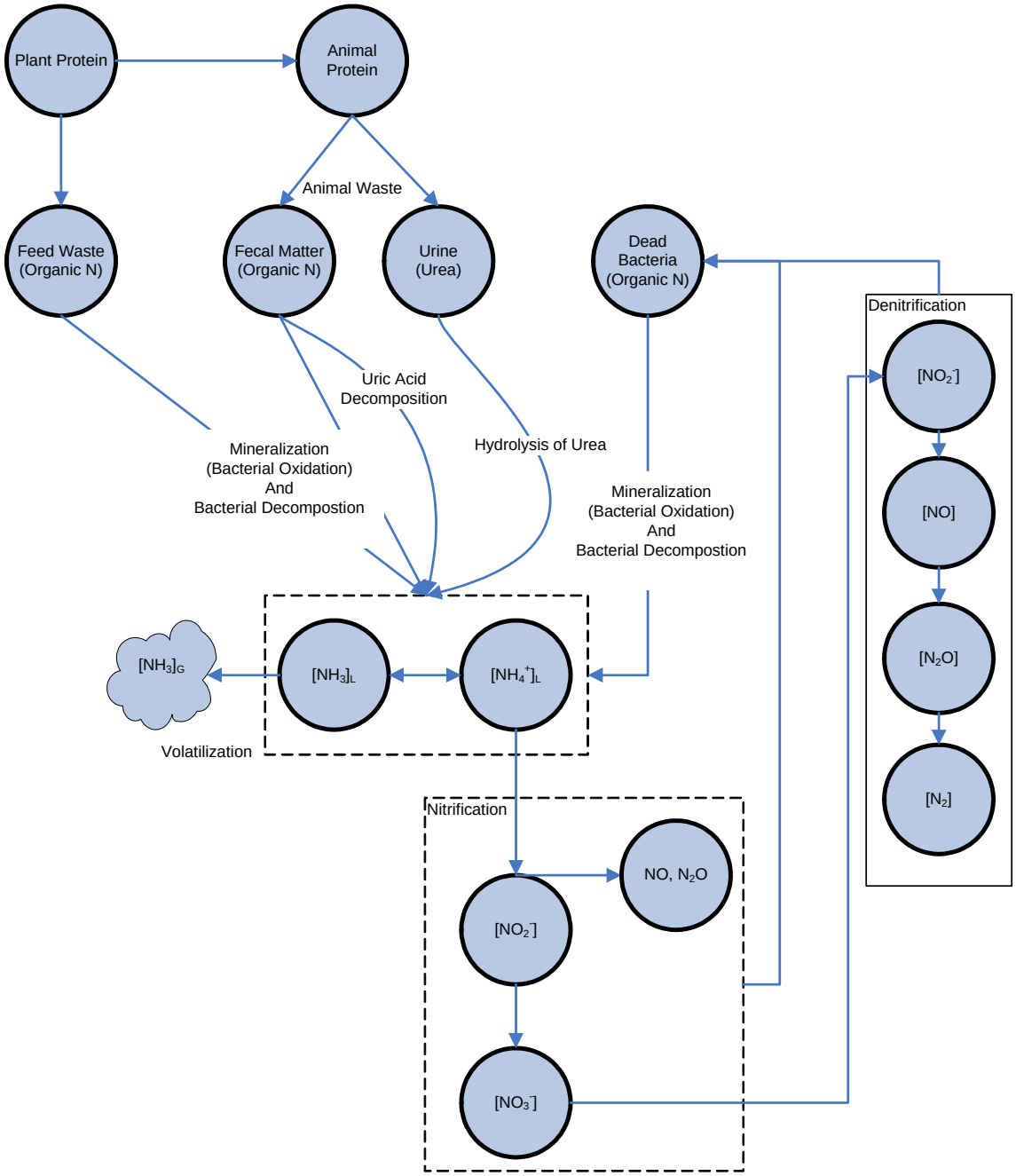


Figure 3.1. Breakdown of animal waste. The breakdown of animal waste is a natural process of the nitrogen cycle. Ammonia, nitrogen oxide, nitrous oxide, nitrogen, and nitrogen dioxide are gaseous products of the breakdown process (USDA, 1992; Takaya et al., 2003; Robertson et al., 1988).

Ammonia is one component of the nitrogen cycle. Animals consume nitrogen as feed. The feed is processed in the animals and waste is excreted as manure and urine. In poultry, the waste is only excreted as manure. Ammonia is a byproduct of the breakdown of urine and organic matter. Urea is the primary ammonia producer from urine. The hydrolysis of urea requires only hours for substantial conversion and only days for complete conversion in the presence of the enzyme urease (Asman, 1992). The hydrolysis of urea is shown in equation 3.1(Rodriguez et al., 2005). Uric acid is found in very small amounts in fecal matter for cattle. Uric acid is the primary ammonia producer in poultry. Uric acid is decomposed aerobically to form ammonia as shown in equation 3.2. Protein in the feed and animal waste is mineralized and decomposed to form ammonia.

Hydrolysis of urea:

$$CO(NH_2)_2 + 3H_2O \xrightarrow{\text{Urease}} CO_2 + 2NH_4^+ + 2OH^- \quad (3.1)$$

Aerobic decomposition of uric acid:

$$C_5H_4O_3N_4 + 1.5O_2 + 4H_2O \rightarrow 5CO_2 + 4NH_3 \quad (3.2)$$

Animal waste may be scraped, flushed, or stored in deep pits. Solids from flushed animal waste may be separated and the liquid waste may be processed in a lagoon. Solids may have a wide range of moisture contents. Ammonia in liquid exists as free ammonia and the ammonium ion as shown in equation 3.3. The dissociation of ammonia is driven by temperature and pH (Ni, 1999). Equation 3.4 shows the equilibrium constant for equation 3.3. Clegg and Whitfield (1995) suggested the equilibrium constant varies with temperature for water as shown in equation 3.5. At a pH of 7, only a small amount of ammonia exists as free ammonia. At a pH of 8, a larger amount of ammonia may exist as free ammonia.

Dissociation of Ammonia in liquid:

$$NH_3 + H^+ \leftrightarrow NH_4^+ \quad (3.3)$$

$$K_d = \frac{10^{-pH}\left[NH_3\right]_L}{\left[NH_4^+\right]_L} \tag{3.4}$$

$$pK_d = \left(0.090387 + \frac{2729.33}{T}\right) \tag{3.5}$$

where:

$$pK_d = -\log_{10} K_d \tag{3.6}$$

K_d = Equilibrium constant

$\left[NH_3\right]_L$ = Concentration in liquid phase of free ammonia

$\left[NH_4^+\right]_L$ = Concentration in liquid phase of ammonium ions

T = Temperature [K]

To understand volatilization of ammonia, the two film theory developed by Lewis and Whitman (1924) may be employed. In the two film theory, three steps of ammonia mass transfer occur: the convective mass transfer from the surface of the gas film to the free air stream, the diffusion across the boundary layer, and diffusion inside the bulk manure. An overall mass transfer coefficient is often used to describe the entire two film theory. Arogo et al. (1999) defined the overall mass transfer coefficient to be a function of air viscosity, diffusivity in air, air velocity, liquid temperature, air temperature, and a characteristic length.

Nitrification is a process where the ammonium ion is oxidized by autotrophic and heterotrophic bacteria to form nitrites and nitrates. Nitrification requires oxygen to form nitrites. The byproducts of autotrophic bacteria are different from the byproducts of heterotrophic bacteria. Autotrophic bacteria exist in aerobic conditions, while heterotrophic bacteria exist in both aerobic and anaerobic conditions. The role of heterotrophic bacteria in the nitrogen cycle is unknown (Robertson et al., 1988).

Denitrification is the sequential reduction of nitrates and nitrites to nitrogen gas. Denitrification may take place aerobically or anaerobically (Robertson et al., 1988). One of the byproducts of the denitrification process is nitrous oxide (Takaya et al., 2003).

Measuring Ammonia in Barns

Barns in AFOs provide a containment structure with necessary shelter from nature's elements. Barns may be classified into naturally ventilated and mechanically ventilated facilities. Ventilation in barns provides multiple functions, including removal of gases, such as ammonia, from the barn while providing clean, fresh air to the animals. Temperature in the barns is regulated in part by changing the ventilation rate of air through the barn. Poultry and pork are often housed in barns. Dairy cattle may be housed in barns or open lots. The frequency of removal of manure from barns varies from one operator to another.

Naturally Ventilated Barns

A naturally ventilated barn is a barn for which the ventilation is driven by non-mechanical forces of wind and buoyancy (Bartali and Wheaton, 1999). In a naturally ventilated barn, the temperature and ventilation rate are controlled by the opening and closing of openings to the building. The exhaust often flows through a ridge opening that spans the top of the roof.

Dairy freestall barns in the southern United States are a type of naturally ventilated barn. Freestall barns are generally more open than other naturally ventilated barns where the temperature needs to be controlled. A concrete floor may be scraped or flushed.

Naturally ventilated barns are particularly difficult to measure because the ventilation rate is often unknown and very difficult to measure. One method of sampling is upwind and downwind sampling. Multiple houses and waste handling are often built for the operation. It is difficult to compare emissions from one house to another.

Mechanically Ventilated Barns

A mechanically ventilated barn is a facility for which the ventilation is driven by fans. In a mechanically ventilated barn, fans may be placed either on one end of the barn or spaced along the sides of a barn. Fans are turned on and off to control the temperature and ventilation rate of the barn. In some hog barns, manure from the pigs drops into a pit under the barn. Several fans are used to draw air across the manure to reduce the concentrations of gases inside the building.

Mechanically ventilated buildings pose several challenges for the measurement of ammonia. Airflow through these building varies seasonally and temporally. For example, the recommended airflow for a layer facility is 0.85 m^3/h/bird (0.5 cfm/bird) in cold weather and 6.8 m^3/h/bird (4 cfm/bird) in warm weather (MWPS, 1983). A typical 25,000 bird broiler house may have ten 1.2 m (48 in) diameter fans. A typical 100,000 bird layer house may have 50 0.9 m (36 in) diameter fans. Fans are typically turned on and off to regulate the airflow. Some newer facilities have adopted variable speed fans.

When sampling mechanically ventilated buildings, selection of the sampled exhaust fans is random (Heber et al., 2001). It is expected that the concentrations leaving the exhaust may not be uniform from one exhaust to another. This depends on the configuration of the house and whether animals were able to bunch in a particular area.

Measuring Ammonia in Open Areas

Open areas may be classified as open lots, manure storage, or compost. Emissions from open lots may be measured by nitrogen mass balance, upwind/downwind concentration measurements, flux enclosure, or trace gas methods. Emissions from open areas are likely to be heterogeneous since animal location and manure accumulation will most likely be heterogeneous.

Open lots

Open lots consist of pens in which animals are held. The surface of most open lots is soil based. Typically feeder cattle and some dairy cattle are held in open lots. Recommended stocking densities of open lots vary by type of animal. Cattle tend to locate in some areas within the lot more than others. Cattle may create craters that collect urine and feces on the pen surface. The surfaces of open lots tend to be heterogeneous in nature ranging in loading and moisture content. Operators have different scrape and fill schedules for open lot pens.

Manure Storage

Manure storage involves solids storage, slurry pits, retention ponds, and lagoons. Much of the solids waste may be removed from flushed manure through the use of solids separation. Scraped manure from open lot pens and barns may be piled until time to land-apply the byproduct. Slurry pits hold high solids content manure. This manure is often land applied using special liquid manure injection systems or with the use of liquid spreaders.

Liquid manure stores may be aerobic, facultative, or anerobic. The byproducts of these bioreactors are dependent on many factors including loading rates, oxygen, pH, temperature, and bacterial condition. Runoff ponds are holding areas for flush water and runoff. Lagoons provide treatment depending on loading rate, manure characteristics, and environmental factors.

Compost

Some AFOs compost manure and hay for a value added product. Compost is typically placed in rows so that it may be turned easily. Compost is turned on a regular basis to improve aeration. During the composting period, compost reaches temperatures of 50-60 °C (Liang et al., 2004).

CHAPTER IV

RESEARCH OBJECTIVES

The goal of this research is to provide the ability to measure emissions of ammonia from AFOs. By providing the ability to measure ammonia effectively, BMPs may be developed to aid operators of AFOs to reduce emissions. Two primary objectives were established to meet the goal of this research:

1. Develop a process based measurement system for analyzing and evaluating BMPs relating to fugitive ammonia emissions from AFOs. The system presented will improve current sampling methods through improved data management, increased sampling rate, and a more user-friendly interface.
2. Evaluate system performance for the given operating conditions to determine if system will meet acceptable criteria. The performance of the system will be tested for uncertainty, system response, and adsorption. The uncertainty of the system is expected to be less than 20% for the given operating parameter. An uncertainty budget of the instrument will be developed to determine system uncertainty. The system response of the instrument is expected to allow for the measurement of ammonia. System response will be modeled to determine the limitations of the system. Adsorption on chamber surfaces is not expected to significantly affect the measurement of concentrations in the chamber. The adsorption kinetics will be tested for the chamber to determine the significance.

CHAPTER V

DEVELOPMENT OF A PROCESS BASED MEASUREMENT SYSTEM

The Center for Agricultural Air Quality Engineering and Science (CAAQES) uses several methods to measure ammonia and hydrogen sulfide from ground level area sources (GLAS). These measurements are primarily taken from AFOs. Generally, CAAQES has used a method detailed by Kienbusch (1986) using emission isolation flux chambers to measure ammonia and hydrogen sulfide emissions. CAAQES had acquired two 17C (Thermo Inc. Franklin, MA) ammonia analyzers, one 45C hydrogen sulfide analyzer, and one 450C hydrogen sulfide analyzer, and required enhanced efficiency of field sampling because of increasing costs. Every field process step was examined to reduce the time of sampling. This study focused on data management, time management, and protocol development. The goal of this work was to present the design a multiplexer system for CAAQES to measure ammonia and hydrogen sulfide more efficiently during field sampling.

Background

The flux chamber method is based upon the two-film model (Jiang & Kaye, 1996). The two film model relates the emission flux of a gas to the concentration of the gas in the liquid using Henry's Law and diffusion. Several factors affect Henry's law and diffusivity, including concentration gradient, temperature, and pressure. These factors are often not addressed by those using the flux chambers.

Humidity can largely affect measured emissions since water can combine with volatilized ammonia. Care must be taken to not increase the temperature of the air in the chamber and sequentially reduce the temperature in the lines since this could result in condensation. Condensation can adversely affect the thermal mass flowmeters as well as the analyzers. The ammonia and hydrogen analyzers are capable of handing water vapor but not liquid water.

While ammonia is of high concern at CAAQES, hydrogen sulfide is also a concern. An analyzer bank consists of one ammonia analyzer and one hydrogen sulfide analyzer. The original system and new system were designed such that both analyzers in the analyzer bank could be used simultaneously.

Original System

Originally, only one flux chamber was used by CAAQES to sample emissions from AFOs. The sampling process took approximately 1 hour to sample plus time to move the flux chamber from one location to another. The flux chamber required 15 minutes to move when sampling a lagoon and approximately 5 minutes to move on dry surfaces. The total time required to obtain a sample was conservatively estimated to be 1 hour 15 minutes.

LabVIEW 5.1 (National Instruments, Austin, TX) was the programming language of choice for the original setup. Three programs were required to obtain data and control the gas flow to and from the chamber. The first program controlled the flow rates using a mass flow controller (MFC series, Aalborg Instruments, Orangeburg, NY) via a DAQCard (AI-16-XE-50, National Instruments, Austin, TX) coupled with two digital to analog converters (Maxim 544, Dallas Semiconductor, Sunnyvale, CA). The second program logged data from the analog outputs of the analyzers every five seconds. Temperature data from the ambient air, flux chamber, and source were also recorded every five seconds. The five second data proved to be cumbersome to analyze and the one minute data was determined to be sufficient for estimating gaseous emissions. The third program provided concentration data from the analyzers via the RS-232 serial port. The digital and analog data were each logged into a file.

Calibration of the analyzers involved attaching a gas cylinder of known concentration to the system. The calibrated gas was mixed with zero air to reduce the concentration of the gas as needed. A static mixer (1/2-80-PFA-12-2, Koflo Corporation, Cary, IL) was used to mix the gas thoroughly. The calibration was performed according to manufacturer's recommendations.

As data collection progressed, a few shortcomings with the original setup became apparent. First, the single chamber only allowed the sensor to be used less than half of the time. This limited the total number of samples to approximately 35 for a 4 day sampling period when sampling 13 hours per day. Data management was also a problem. Data was lost and was difficult to manage because of the multiple program structure. The non-integrated program structure was also difficult for the user to navigate.

The method of flux chamber sampling is described in detail by Kienbusch (1986) in *Measurement of Gaseous Emission Rates from Land Surfaces Using Isolation Flux Chamber*. The CAAQES protocol follows this method. Upon arriving at the AFO, the site is divided into various manure handling, storage, treatment, and animal confinement units. This identifies areas emitting the measured gases. For example, a dairy in Central Texas may be divided into freestall, open lot, solids separation, lagoon, and composting areas. Each of these units is further divided into random samples. The number of samples depends on the total surface area and consistency of the area. Statistical analysis was used to determine the number of samples required for each unit.

The flux chamber used by CAAQES has a diameter of 0.495 m, a cylinder height of 0.24 m, and hemispherical top with height of 0.17 m as shown in figure 5.1. The cylinder was manufactured of 10 ga. AISI 304 stainless steel for durability and chemical resistance. The hemispherical top, inlet tube, and outlet tube were purchased from Odotech Inc. (Montreal, Quebec). The inlet and outlet tubes were made of PerFluoroAlkoxy (PFA). The hemispherical dome was manufactured of acrylic. The chamber has a volume of 65 L.

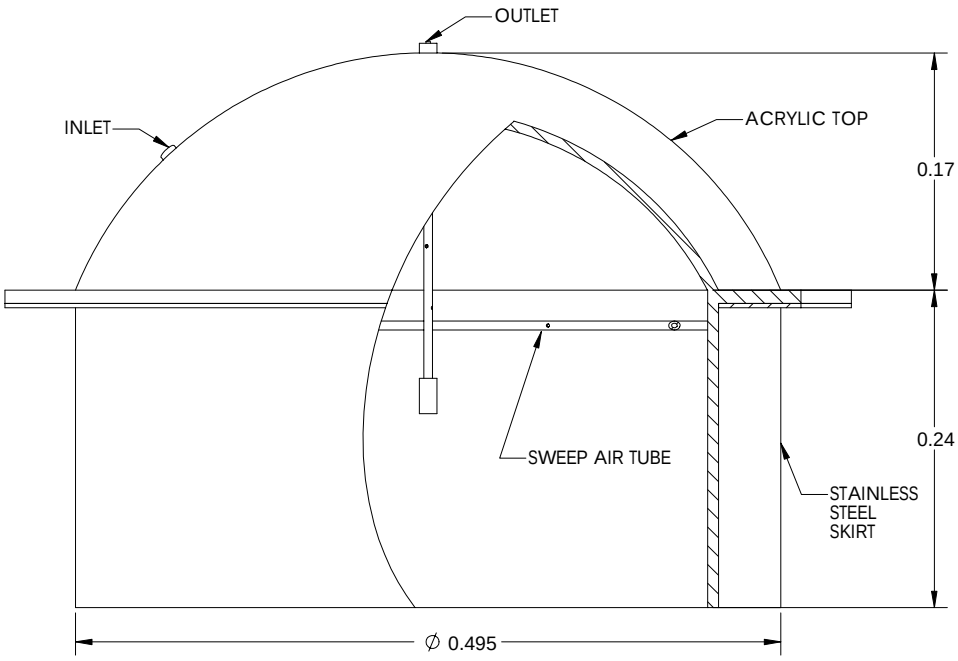


Figure 5.1. Schematic of the flux sampling chamber used by CAAQES.

The sampling process begins when the chamber is placed on the GLAS. A flow rate of 7 L/min (21°C, 1atm) of zero air from a gas cylinder or zero air generator (737-12A, AADCO, Village of Cleves, OH) is pumped into the chamber as a sweep air. Zero air is air that has been purified to remove pollutant gases. Two to four liters per minute (21°C, 1 atm) are drawn from the chamber and the flow is split into one hydrogen sulfide analyzer and one ammonia analyzer. The chamber is vented to the atmosphere so that the remaining gas exits the chamber. The chamber is flushed for thirty minutes followed by thirty minutes of sampling.

Goals

A new integrated system was proposed for which analyzer downtime was almost zero. The new system multiplexed three chambers for each set of ammonia and hydrogen sulfide analyzers. This allowed the analyzers to be used continuously throughout the sampling trip. The system allowed collection of over 80 samples during

a four day sampling period from a single analyzer at an average rate of 1.33 samples per hour including system setup and takedown each day. Because of the increased amount of data received from the analyzers, a good data management system was essential.

The multiplexer system allowed multiple receptors to be sampled using a single analyzer. Three chambers could be placed on an emitting source and samples taken sequentially. Figure 5.2 shows a diagram of the multiplexed chamber setup placed in a field setting.

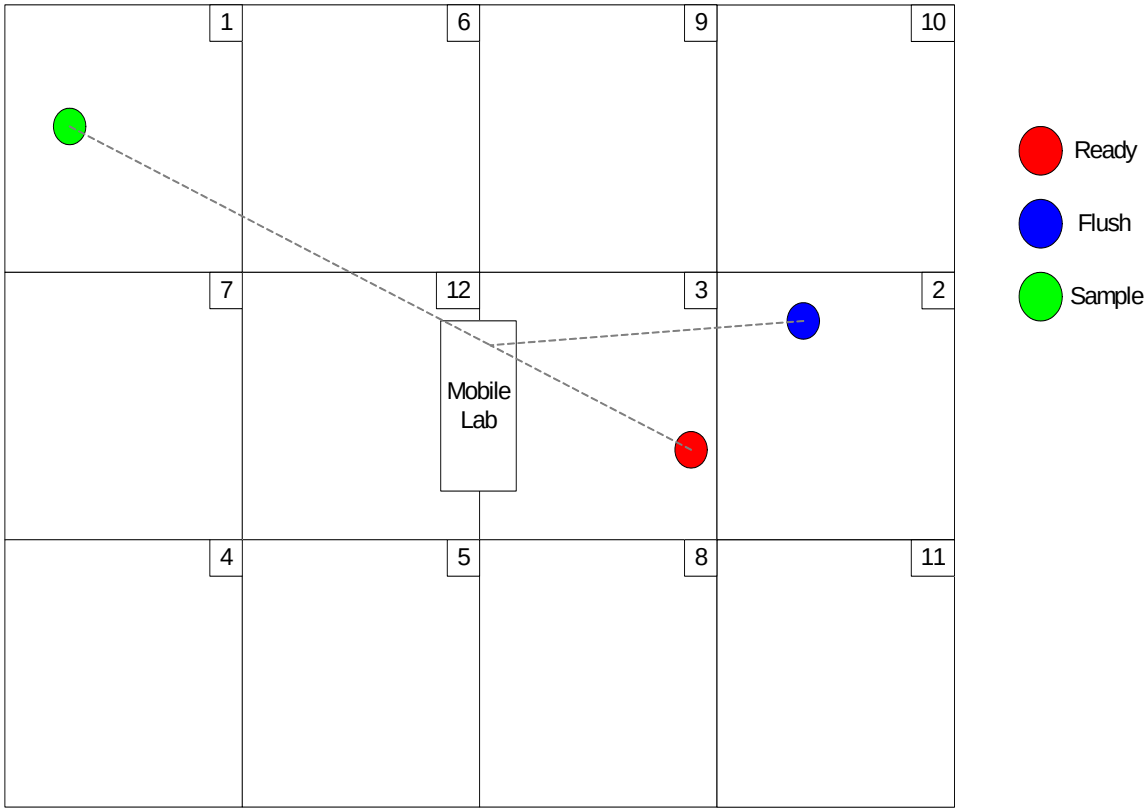


Figure 5.2. Multiplexed chamber setup. The mobile lab is placed near the center of the sampling area. Three flux chambers are placed in random locations within a sample area grid. Grid areas are chosen at random with respect to time. Flux chambers are sampled sequentially by the analyzer with the use of the multiplexer.

The multiplexer system controls three major processes: zero air flow, sample flow, and chamber lift. Figure 5.3 shows one chamber with the major control processes. The chamber must be lowered at the beginning of each test. After the chamber is

lowered, the zero air flow begins and remains until the end of the sample. The chamber is flushed for 30 minutes followed by a 30 minute sample. The chamber is flushed to remove effects due to the response time of the chamber. The chamber is lifted at the end of the sample so that it may be relocated for the next sample.

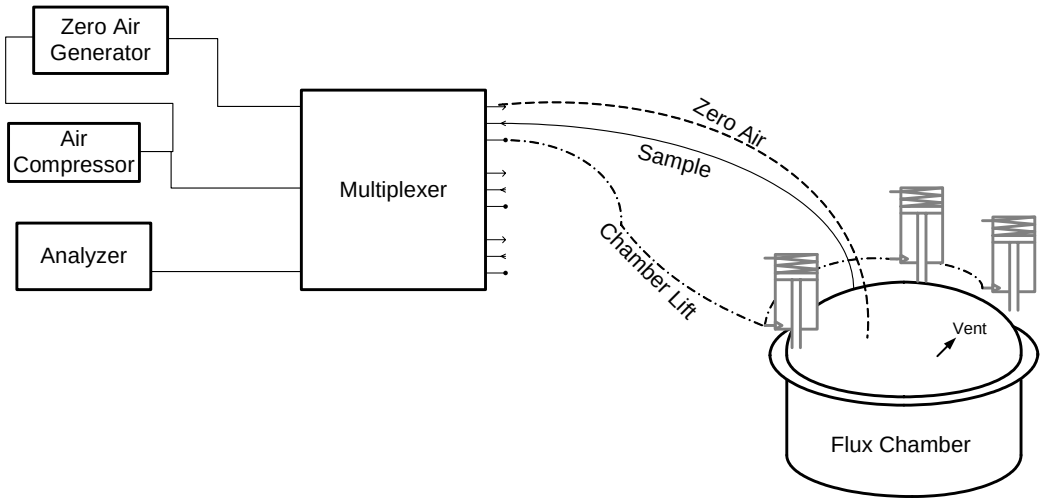


Figure 5.3. Multiplexer control of chamber. The multiplexer controls the chamber lift, sample flow, and zero air flow. An air compressor supplies air for the chamber lift. A zero air generator provides zero air for the chamber.

The multiplexer control included a series of solenoid valves (Gold Ring Series 20, Parker Hannifin Corp., Madison, MS) that open and close to calibrate, run and flush the system. These valves were controlled via Fieldpoint modules (National Instruments, Austin, TX). LabVIEW 7.1 software was used as the control interface for the Fieldpoint modules. Mass flow controllers (MFC series, Aalborg Instruments, Orangeburg, NY) were used to adjust the zero air flow rate entering the chamber. Needle valves (#06393-80, Cole-Parmer, Chicago, IL) were used with mass flow meters (MFM series, Aalborg Instruments, Orangeburg, NY) to adjust the flow of air to be analyzed.

A schematic of the control system is presented in Figure 5.4. Chambers were controlled by a pneumatic lift mechanism to lower the individual chamber at the beginning of the test and raise the chamber at the end of the test. All of the chambers were initially in the upward position with S18, S20, and S22 open (figure 5.4). An air

compressor and pneumatic cylinders provided the force to lift the chambers. When the chamber was ready for sampling, it was lowered by releasing the pressure in the lines by opening S19, S21, or S23 (figure 5.4).

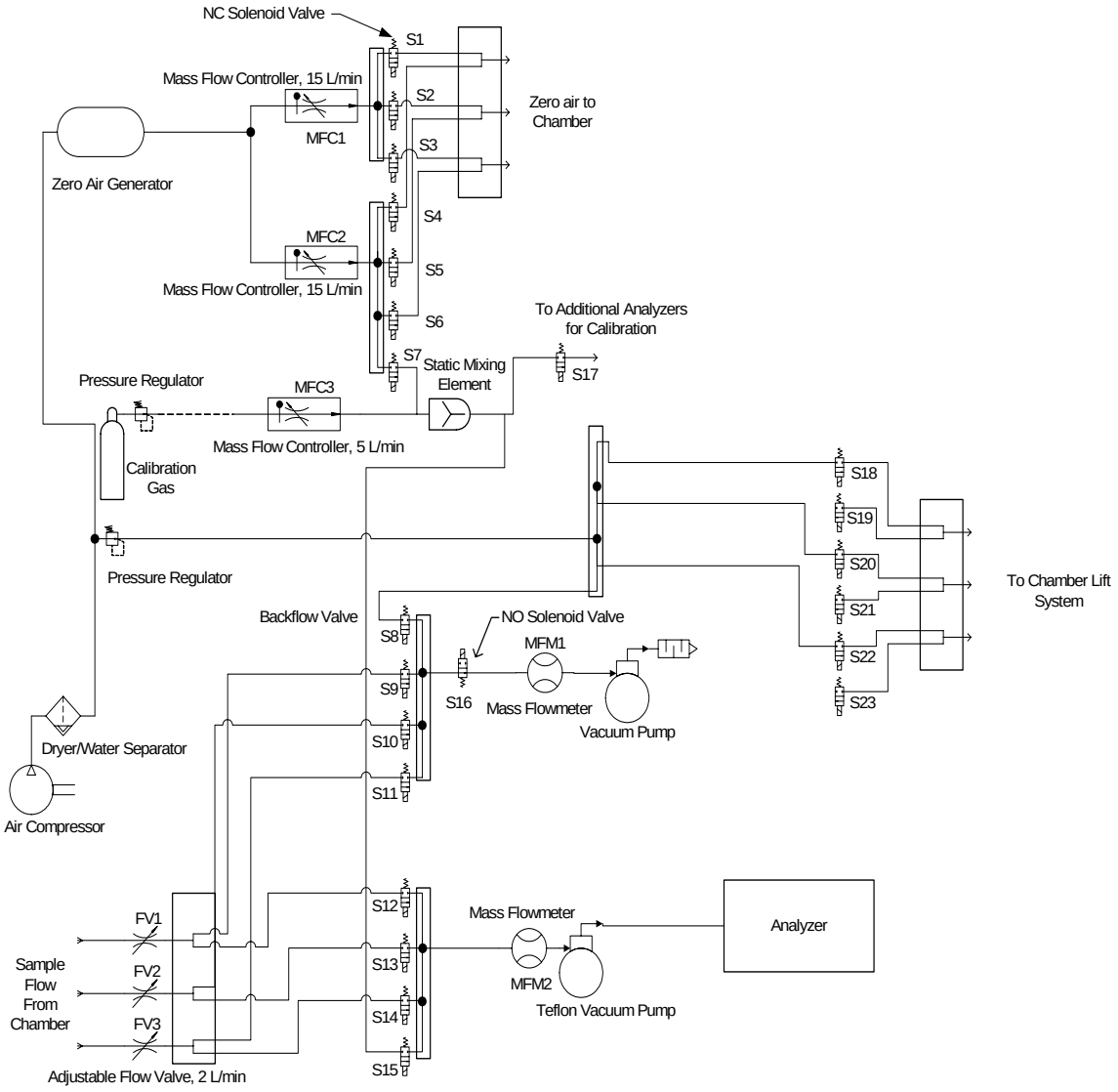


Figure 5.4. Multiplexer schematic. The multiplexer controls zero air flow, sample flow, and pneumatic lift. Additional multiplexers may be calibrated with the use of valve S17. Mass flow controllers automatically control the flow. The mass flow meters measure the sample flow from the chamber. Solenoid valves control the flow to each chamber.

Only two of the three chambers were used at any given time. Two mass flow controllers (MFC1& MFC2, figure 5.4) were used to control the zero air flow rate into the chambers. Manifolds and six solenoid valves (S1-S6, figure 5.4) were used to distribute the zero air to the respective flux chambers.

Air from the chambers was drawn through Teflon PFA tubing into the enclosure where it was metered using a needle control valve (FV1-FV3, figure 5.4). Six solenoid valves (S9-S14, figure 5.4) controlled the path of flow. The valves were place in the off position when the chamber was inactive. Two flow paths may be chosen if the chamber was active depending whether the chamber was in flush mode or was in sample mode. A standard duty vacuum pump (117CAB18, Thomas Industries, Louisville, KY) maintained the flow during flushing (first 30 minutes). A second vacuum pump (N810FTP, KNF Neuberger, Inc., Trenton, NJ) drew the flow to the analyzer during the sampling period. A mass flow meter (MFM1 & MFM2, figure 5.4) indicated the flow rate from the chamber.

A gas dilution system was incorporated into the multiplexer for calibration of the analyzers. Flow of regulated calibration gas was controlled with a mass flow controller (MFC3, figure 5.4). Zero air flow was controlled by MFC2 and S7. The zero air and calibration gas are mixed using a static mixing element (1/2-80-PFA-12-2, Koflo Corporation, Cary, IL). Since only one calibration system is required for both analyzer banks, a solenoid valve (S17) is available for the calibration of the second analyzer.

Multiplexer Programming

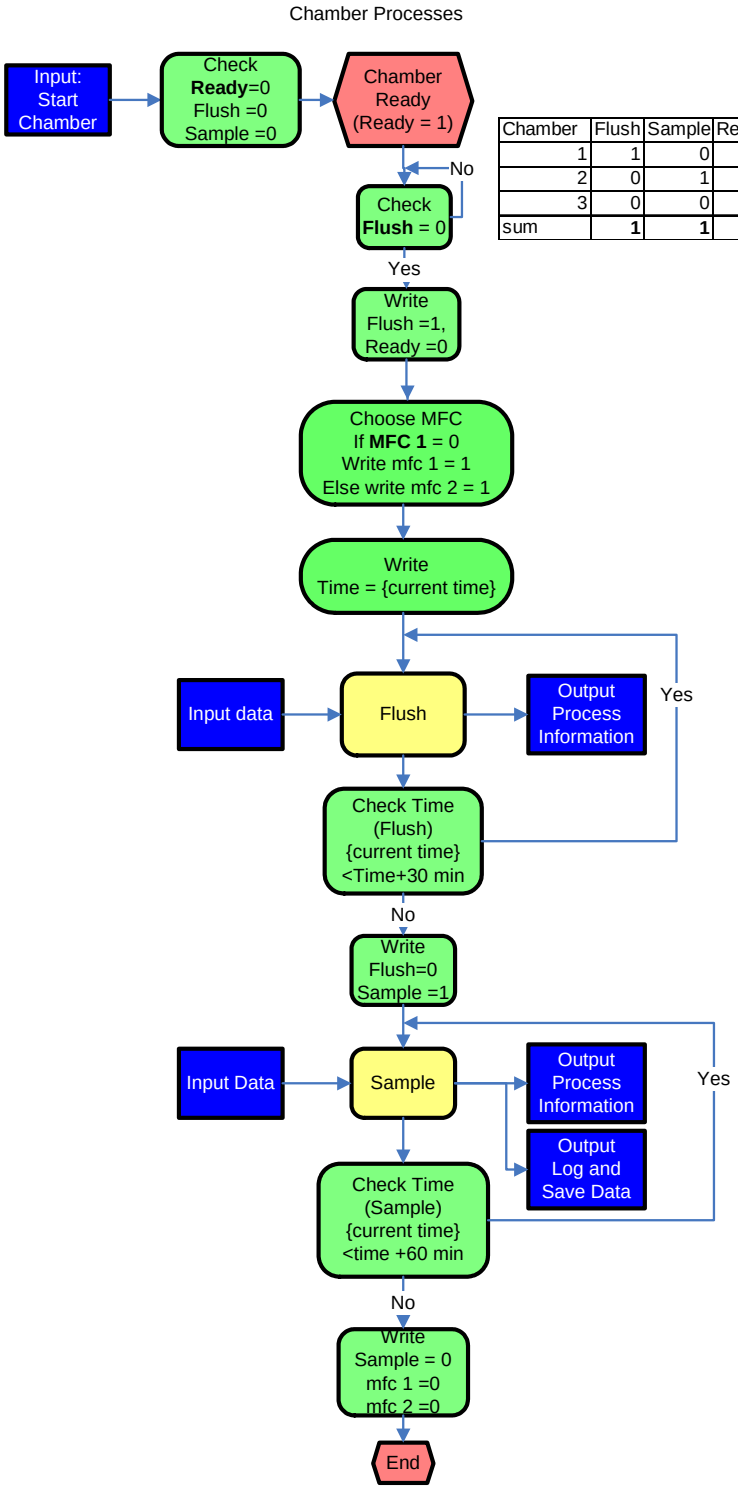
The multiplexer program may be divided into several areas. The subprograms are designed to be modular so that the measurement system may be used with other sampling methods. Programming of the multiplexer system is performed in LabVIEW 7.1 (National Instruments, Austin, TX). Details of the subprograms are presented in appendix A.

Flux Chamber Sampling

The process structure of the multiplexer used in conjunction with sampling flux chambers is shown in figure 5.5 illustrating the important steps in programming the multiplexer. The data structure is presented in the top right of the flow diagram. In the data structure, a "1" indicates the component referring to the variable is active and a "0" indicates that the component is not active. The bold variables indicate the sum of the column in the data structure. To begin the process, a user pressed a button that activated the chamber after it was positioned. The program checked the status of the chamber to see if it was in queue or in flushing/sampling mode. This was done by checking the variables: ready (sum), flush, and sample. If all variables were inactive, the ready variable for the individual chamber was activated. Nothing happened if any of the variables were active. The program continuously checked to see whether any chamber changed from flush mode to sample mode. A chamber moved from flush mode to sample mode after 30 minutes. The mass flow controllers were multiplexed such that each flow controller was used at all times when multiple chambers were active. To preserve the flow integrity, the same flow controller was used throughout a flush and sample period for a chamber. At 60 minutes, the sampling was completed and the variables were reset for the chamber.

Calibration

Calibration of the analyzers was performed by a dilution system. In this system calibrated gases were diluted to the required level for multipoint calibration. Calibration procedure was followed according to manufacturer's specifications as outlined in the instruction manuals.



Chamber	Flush	Sample	Ready	mfc1	mfc2	T(chamber)
1	1	0	0	0	1	8:30
2	0	1	0	1	0	8:00
3	0	0	0	0	0	
sum	**1**	**1**	**0**	**1**	**1**	

Figure 5.5. Multiplexer process diagram. Only a chamber that is not in flush or sample mode may enter an empty queue. A chamber in flush mode enters sampling mode when the sampled chamber completes sampling. A chamber enters flush mode after the flushed chamber enters sample mode.

Error Checking

Checking for errors is an important part of any complex system. The program enabled the system to check for flow rate errors and alerted the user of the error as it occurred. The error checking had several levels of errors. If an error was severe enough, the chamber was stopped and allowed to begin again. Before each sampling period, the sample lines were flushed to ensure that no condensation remained in the line from the previous sample. This was one method to reduce the chance of damaging a mass flow meter or mass flow controller.

Data Acquisition

Data acquisition is an important function of the instrumentation. Data from the analyzers was logged as well as temperatures from the chambers. Temperatures were logged using data loggers (HOBO H08-008-04 with TMC6-HC temperature probes, Onset, Pocasset, MA) that were placed on each chamber. The temperature inside the chamber, outside the chamber, and from the source were measured each minute. Relative humidity was logged on two of the six chambers. Data was downloaded from the data loggers every 24 hours to a computer using serial digital interface and BoxCar Pro software (Onset, Pocasset, MA). Temperature data was exported to a tab delimited text file for input in a spreadsheet or database. One minute concentration averages were output from the analyzers using a serial digital interface through LabVIEW. Flowmeter data and concentration data were saved to a comma delimited text file.

User Interface

A user interface was provided for the user. The user interface consisted of a 5.7" touchscreen panel (TPC-642SE-CE, Advantech, Cincinnati, OH), three momentary on selector switches and three momentary on push button switches. The touchscreen panel allowed users to view system status including concentrations, chamber status, system errors, flowrates. Users input the sampling source by using the touchscreen. The selector switches were used to activate the particular chamber. An indicator light in the switch indicated whether the chamber was active. Once the chamber was active, a push

button was pressed to place the chamber in queue. Figure 5.6 shows the user interface of the multiplexer.

Figure 5.6. User interface of the multiplexer. The interface consists of: selector switches to activate each chamber, push button switches to place a chamber in queue, and a touchscreen to display pertinent data.

Data Management

Data management plays a key role in the sampling trips. Data flow through the system is presented in figure 5.7. Temperature was logged by the data loggers (HOBO H08-008-04 with TMC6-HC temperature probes, Onset, Pocasset, MA) and downloaded to a computer. Flowmeter and concentration data were logged and saved to a flash data card located in the touch screen. The data was downloaded to a computer by using an USB link to a computer and ActiveSync software (Microsoft, Redmond, WA).

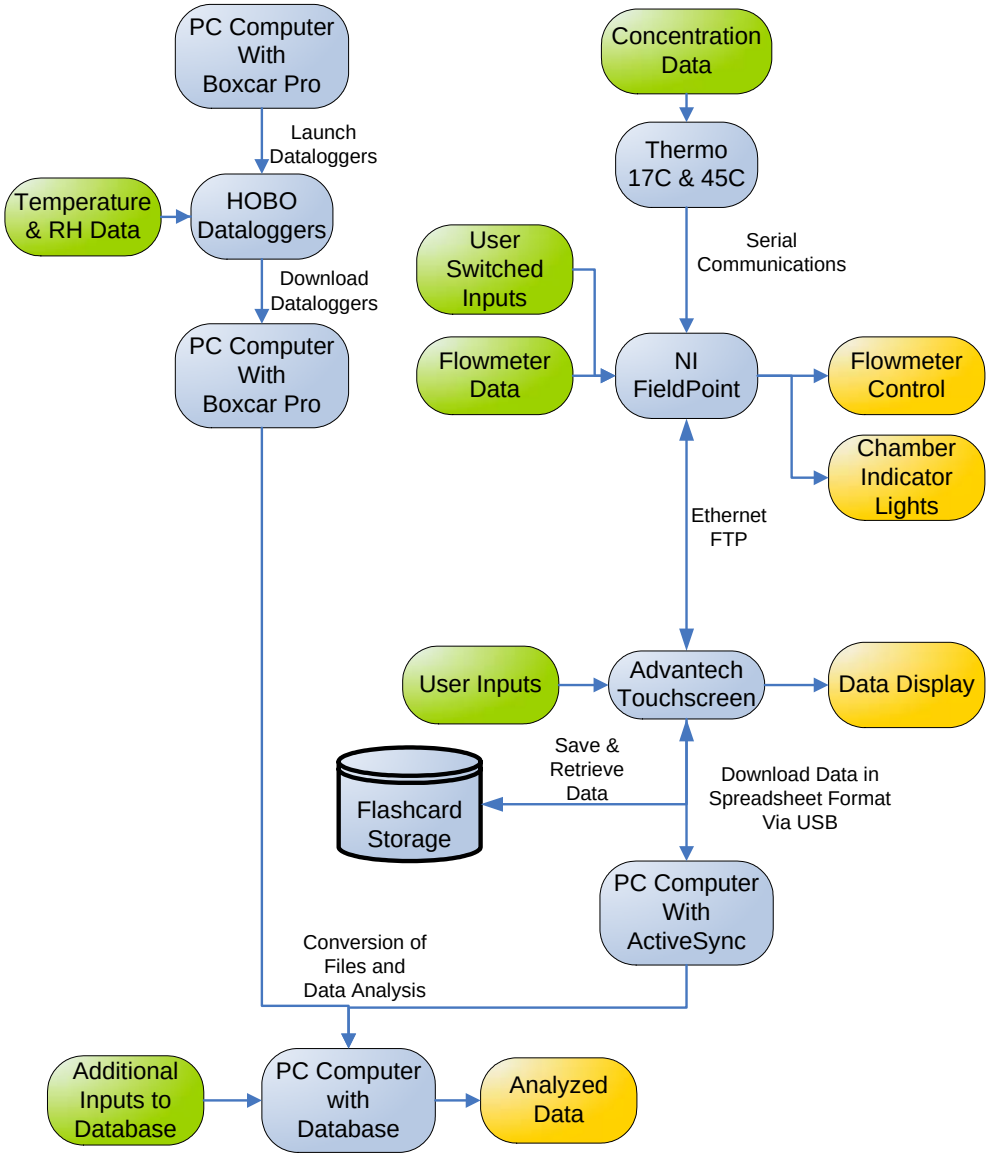


Figure 5.7. Data flow through the sampling system. Dataloggers record temperature and relative humidity data. The NI FieldPoint modules collect flowrate and concentration data and sent the data to the touchscreen where it is saved on flashcard storage. Data is downloaded from the touchscreen and dataloggers for further analysis.

Enclosure

Aluminum enclosures were built to house the components of the multiplexer as well as the analyzers. Each enclosure was built so that it could be pulled with an all terrain vehicle. This allowed the two analyzer banks to be positioned up to 50 m apart. The enclosures were sized to contain a standard rack system and included an area for

attachment of the multiplexer system. In the rear of each enclosure, user controls, power connections, and flow connections were positioned for easy access. A side door was designed to be fully removable for access to the equipment inside each enclosure. The enclosures were insulated and air conditioned to keep the equipment at the proper temperature. Figure 5.8 shows the enclosure with the side door removed.

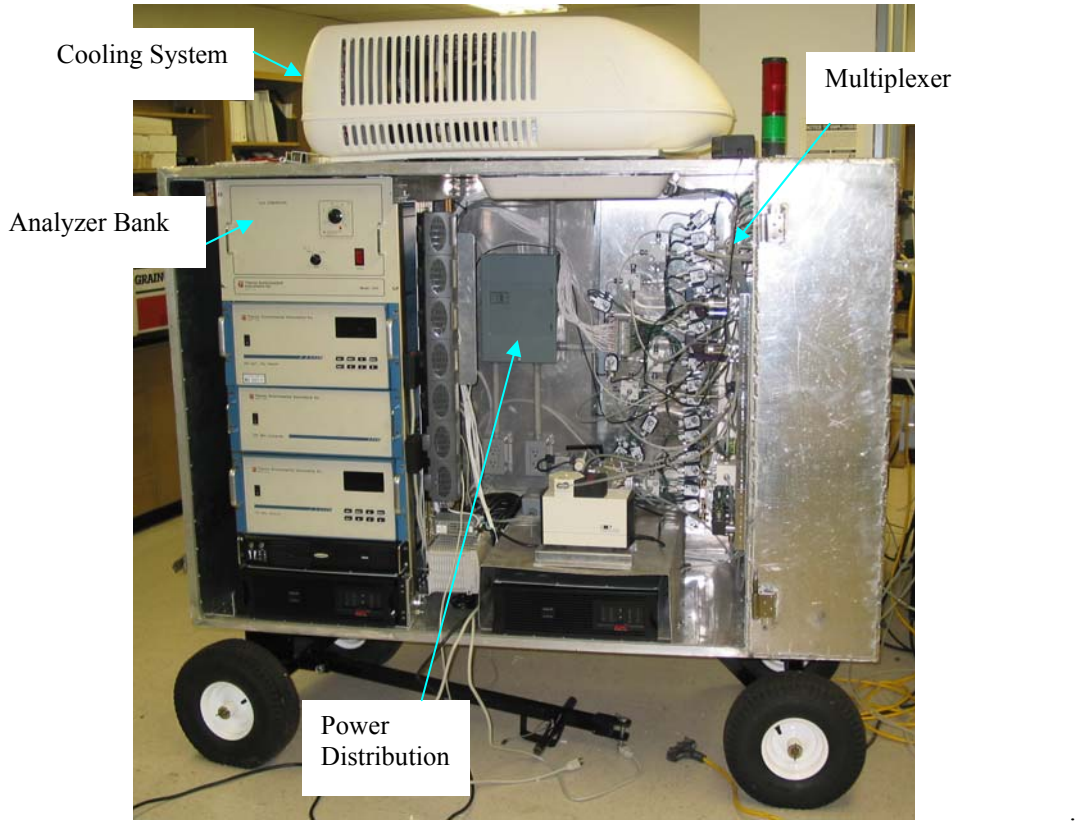


Figure 5.8. Enclosure with side door removed. Components are placed for easy access in the enclosure. Each enclosure contains an analyzer test bank, power distribution system, multiplexer with flowmeters, and cooling system.

Summary

The new system increased the number of samples taken, allowed better retention of data and was easier to use. This increased productivity for the sampling period. Although the multiplexer system was designed to operate with chambers, it may have other uses in field and laboratory sampling of air pollutants. CAAQES can currently

obtain over 90 samples per day with two analyzer banks and multiplexers when working 24 hours per day.

Future Improvements

Several improvements can still be made to the enclosure system including tubing management and replacement dataloggers. Tubing may become entangled in the feet of cattle in the open lots and free stalls, resulting in a broken line. Additionally several wrenches are required to attach and detach the chambers. Tubing may be managed by providing quick disconnects, covering the lines, and limiting the amount of excess line run out.

Current dataloggers do not allow for integrated data management. Temperature and relative humidity is logged separately from the concentration and flowrate data. Additionally, some problems have been found with data integrity of the current dataloggers. This problem has been identified as a faulty connection between the datalogger and temperature sensor. The sensor may become partially disconnected without the user knowing resulting in the entire data set being lost for that datalogger.

CHAPTER VI

PERFORMANCE OF THE SYSTEM: UNCERTAINTY

Scientists, engineers, and policy makers must understand the reliability of air quality data. In particular, scientists and engineers working in the air quality sector use the reliability of data in determining emissions. The data must be reported with uncertainty limits so that practitioners can understand and use what was learned from the study. Policy makers must understand the credibility of the data in order to make sound policy decisions.

One method of showing the reliability of data is by reporting the uncertainty. Uncertainty is defined as the interval about the measurement or result that contains the true value for a given confidence interval (ASME, 1998). Uncertainty arises as a result of random errors. Measurement uncertainty may be grouped into two main categories: those evaluated by statistical methods and those evaluated by other means. These groups are often referred to as type A and type B, respectively.

An error is defined as the difference between an individual result and the true value (Eurachem/Citac, 2000). The error for a specific measurement cannot be known exactly. A system may have a large uncertainty, yet a particular measurement with the instrument may have a small random error value. For this reason, a statistical distribution is often applied to a collection of errors. Three types of error are involved in measurement systems. Random errors arise from unpredictable variations in the quantity measured. These errors give rise to variations in repeated observations of a measurand. Uncertainty is a result of random error. Systematic errors arise from factors that create a shift in the measured quantity from the actual quantity. Systematic errors are independent of the number of observations. Systematic errors may be constant over a range or vary in a predictable manner. Bias is a result of systematic error and can be corrected through calibration. Spurious error is an error which invalidates the

measurement. This error arises from instrument malfunction or human error. Lost or invalid samples are a result of spurious error.

Every engineering system has uncertainty associated with it. In gas sampling, uncertainty is often associated with instrumentation and flow. One focus at the Center of Agricultural Air Quality Engineering and Science (CAAQES) at Texas A&M University is the maintenance of uncertainty budget for all air pollution sampling equipment. The uncertainty budget is one component in a quality assurance and quality control (QA/QC) plan.

Flux chambers have been used by several researchers to determine gaseous emissions. Kienbusch (1986) developed a user's guide for the use of an isolation flux chamber. Purified air (zero-air) is pumped into the chamber at a set flow rate by means of the zero-air stream. At the same time, polluted air is extracted by means of the sample stream. The sample stream flow rate is less than the zero-air stream flow rate. The differential flow is vented through the top of the chamber to insure that a positive flow out of the chamber vent occurs.

In the CAAQES protocol, the zero-air flow is set at 7 sL/min and the sample flow at 2 to 4 L/min. The simplified sampling setup is presented in figure 6.1. The sample is extracted from the chamber using a vacuum pump (N810FTP, KNF Neuberger, Inc., Trenton, NJ). The vacuum pump supplies the required flow rate of 2 L/min to the analyzer sensor. Zero-air is generated by purifying compressed air with a zero-air generator (737-12, AADCO Instruments, Village of Cleaves, OH). The air is compressed using a oil-less scroll air compressor (SF-2, Atlas-Copco, Holyoke, MA). A chemiluminescence analyzer (17C, Thermo Corp., Franklin MA) is used to measure the concentration of ammonia in the chamber. The ammonia analyzer requires that the input pressure be atmospheric so a vent tube was attached according to manufacturer's recommendations (Thermo, 2002a). Standard ranges for the analyzer have a maximum span of 20 ppm. The analyzer may be operated with extended ranges with spans to 100 ppm.

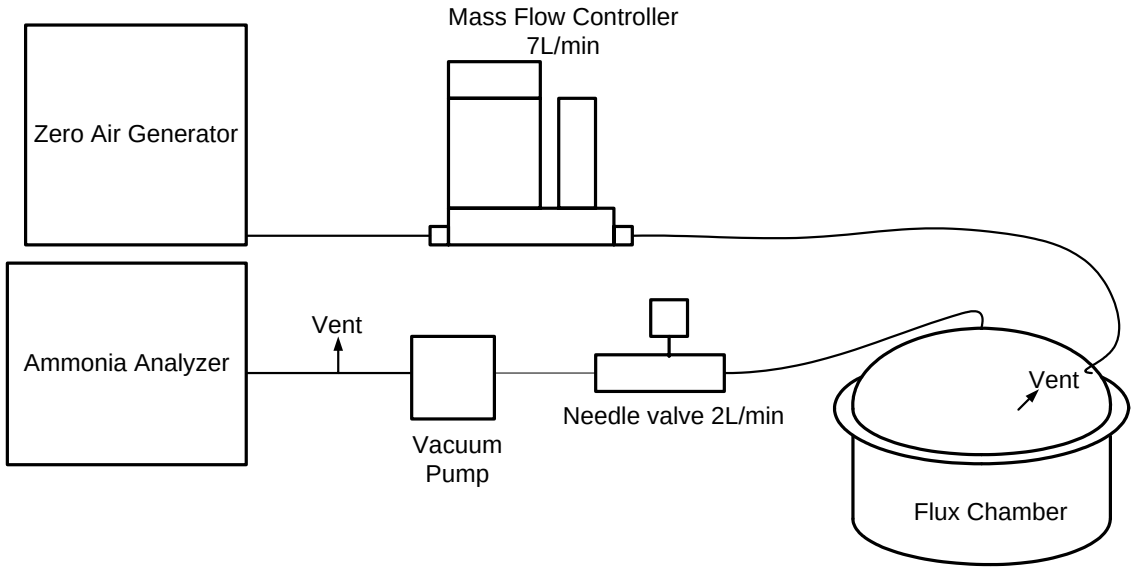


Figure 6.1. Ammonia analyzer setup. Zero air is pumped into the flux chamber at 7 L/min, and 2 L/min are extracted from the chamber to be sampled. Flow to the chamber is controlled by a mass flow controller, and flow from the chamber is controlled by a needle valve.

The 17C instruction manual provides details regarding the analyzer instrument calculations (Thermo, 2002a). A simplified set of equations used by the analyzer are presented in equations 6.1 – 6.10. The chemiluminescence analyzer measures the luminescence produced by reacting nitric oxide (NO) with ozone (O_3). The reaction produces light which is directly proportional to the concentration of NO. The reaction is shown in equation 6.1. The NO concentration is corrected using the zero and span correction factors as shown in equation 6.2.

When the analyzer is set to automatic mode, the multiplexer solenoids sequentially switch between measurements of NO, nitrogen oxides (NO_x), and total nitrogen (N_t) to obtain the concentrations of NH_3 and nitrogen dioxide (NO_2). Each switch of the solenoid is followed by 3 seconds of stabilization and 7 seconds of measurement. NO_x is converted to nitric oxide in a molybdenum converter heated to approximately 325°C. The analyzer sensor measures the resulting luminescence produced by the converted NO_x. The NO_x values are partially corrected using the zero and span correction factors as shown in equation 6.3. The NO_2 concentration is found

by subtracting the partially corrected NO_x concentration from the corrected NO concentration and correcting for converter efficiency as shown in equation 6.4. The NO_x concentration is fully corrected by adding the corrected NO_2 and NO concentrations as shown in equation 6.5. Total nitrogen is converted to nitric oxide in a stainless steel converter heated to approximately 750°C. The analyzer sensor measures the resulting luminescence produced by the converted N_t. The N_t values are partially corrected using the zero and span correction factors as shown in equation 6.6. The corrected NO_x concentration measured in the N_t cycle is fully corrected as shown in equations 6.7 and 6.8. The NH_3 concentration is found by subtracting the partially corrected N_t concentration from the corrected NO_x concentration and correcting for converter efficiency as shown in equation 6.9. The N_t concentration is fully corrected by adding the corrected NH_3 and NO_x concentrations as shown in equation 6.10.

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu \tag{6.1}$$

$$[NO] = a_1 \left([x]_{NO} - b_1\right) \tag{6.2}$$

$$[NO_x]_p = a_2 \left([x]_{NO_x} - b_2\right) \tag{6.3}$$

$$[NO_2] = a_4 \left([NO_x]_p - [NO]\right) \tag{6.4}$$

$$[NO_x] = [NO_2] + [NO] \tag{6.5}$$

$$[N_t]_p = a_3 \left([x]_{N_t} - b_3\right) \tag{6.6}$$

$$[NO_{2a}] = a_5 \left([NO_{xa}]_p - [NO]\right) \tag{6.7}$$

$$[NO_{xa}] = [NO_{2a}] + [NO] \tag{6.8}$$

$$[NH_3] = a_6 \left([N_t]_p - [NO_{xa}]\right) \tag{6.9}$$

$$[N_t] = [NH_3] + [NO_x] \tag{6.10}$$

where:

[NO] = concentration reading of NO {ppb}

[NO_x] = concentration reading of NO_x converted in molybdenum converter {ppb}

[NO_2] = Concentration reading of NO_2 converted in molybdenum converter {ppb}

[NO_x]=Concentration of NO_x converted in SS converter {ppb}

[NO_{2a}]=Concentration of NO_2 converted in SS converter {ppb}

[N_t] = Concentration reading of N_t {ppb}

[NH_3] = concentration reading of NH_3 {ppb}

[x] = uncorrected concentration of input gas {ppb}

a_n = Span correction factors where n=1,…,6

b_n = Zero correction factors where n=1,2,3

subscript p indicates that the concentration has been partially corrected

The span and zero correction factors for the NO, NO_x, and N_t consist of temperature corrections and calibration factors. The span correction factors for NO_2 and NH_3 consist of converter efficiency corrections and calibration factors.

The calibration setup for the analyzer consisted of two mass flow controllers (GFC 17, Aalborg, Orangeburg, NY) that control the zero air and calibration gas flow rates. A static mixing tube (½-80-PFA-12-2, Koflo, Cary, IL) was used to insure that the calibration and zero air were well mixed. Calibration was performed with a flowrate of 12 L/min. Figure 6.2 shows the simplified calibration setup for an analyzer.

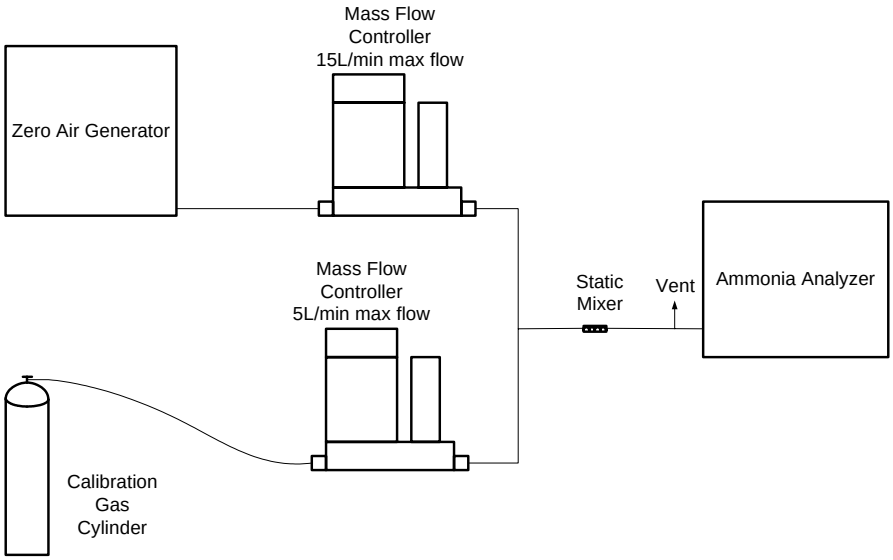


Figure 6.2. Calibration setup for ammonia analyzer

The standard operating procedure (SOP) used to calibrate is outlined in the 17C Instruction manual (Thermo, 2002a). The zero point was calibrated first, followed by each of the individual calibration gases. Each calibration gas (NO, NO_2, and NH_3; Praxair, Los Angeles, CA) had a concentration of approximately 50 ppm, an uncertainty of 2%, and was balanced with nitrogen. The calibration gases were used to calibrate in the 50 ppm span range.

Calibration checks of the chemiluminescence analyzer were performed on a weekly basis. For each check, the analyzers were single point calibrated at 80% of the span (maximum set point) onsite with each piece of equipment running for at least 24 hours before calibration. This assured that the zero-air generator was properly purifying the air and all instruments were stabilized. Multipoint calibrations were completed before and after each sampling venue or once per month (whichever was less). The multipoint calibration was performed using concentrations of 20%, 40%, 60%, and 80% of the span. Each calibration stage was run until the values have stabilized for more than 10 consecutive readings. At least 20% zero-air was input into the analyzer when calibrating. This allowed oxygen to enter the converters to allow the reactions to take place.

System biases include system response and concentration biases in the chamber. Each of the biases is likely to have some uncertainty surrounding the correction factor. The concentration biases within the chamber and tubing include ammonia emission suppression, adsorption, and interferences. Results from Mukhtar et al. (2003) showed that bias due to adsorption of ammonia on polymer tubing was negligible. Work by Capareda et. al (2005) indicated that adsorption of ammonia on the chamber constituted less than an 8% negative bias. The response time of the system is a bias that is minimized as the system reaches stability. Measurements taken in the stabilizing range must be corrected for the system response. The chamber is a form of a continuously stirred tank reactor (CSTR). Therefore the chamber represents a first order response. The ammonia concentration at a given time is defined as

$$C(t) = C_0 + C_\infty (1 - \exp(t/\tau)) \tag{6.11}$$

Where:

C(t) = concentration at time t

C_0 =concentration at time t=0

C_∞ = Concentration after system reaches stability

t =time

τ = time constant

Both biases and uncertainties exist within the sampling and analyzing systems. These biases and uncertainties can be part of the entire system or just the instrumentation. System biases include analyzer constants and analyzer response. Uncertainties from the system arise from instrumentation, calibration gases, data analysis and processing, presentation and interpretation of results, and uncertainty in correction factors.

The reported uncertainty on datasheets often represents a 95% confidence interval. This corresponds to the range of values two standard deviations from the mean. The standard uncertainty for a normal distribution is one half of the reported uncertainty

(Eurachem/CITAC, 2000). The standard uncertainty represents the range of values one standard deviation from the mean. For the calibration gas, the accuracy may be represented by a rectangular distribution. This gives a more conservative estimate of the uncertainty. The standard uncertainty for a rectangular distribution is $1/\sqrt{3}$ of the reported uncertainty (Eurachem/CITAC, 2000).

The objective of this paper is to perform an instrumentation uncertainty analysis of a sampling setup used to measure ammonia emissions. By analyzing the uncertainty budget, areas for which uncertainty can be reduced may be identified.

Methods

The process of uncertainty analysis allowed the combined uncertainty to be estimated. Several steps were involved including: specifying the measurand, identifying sources of uncertainty, quantifying uncertainty, and calculating the combined uncertainty. *Quantifying Uncertainty in Analytical Measurement* was used as a guide for the uncertainty analysis (Eurachem/CITAC, 2000).

Specifying the Measurand

Specifying the measurand involved identifying the methods and procedures used in calibration as well as in sampling. The calibration procedure for the ammonia sampler is presented in figure 6.3. The sampler and zero air generator were run at least 24-h prior to calibration. The proper measurement ranges of the sampler were selected. The zero was calibrated by passing zero air to the sampler and selecting the zero coefficients. The NO, NO_x, and N_t coefficients were set after passing the NO calibration gas through the sampler. The NO_x conversion efficiency was calibrated by passing NO_2 calibration gas to the sampler. The N_t converter efficiency was calibrated by passing NH_3 calibration gas to the sampler.

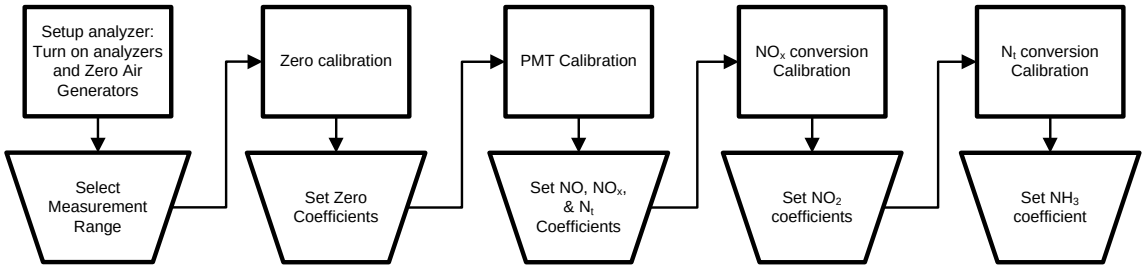


Figure 6.3. Calibration procedure for NH_3 chemiluminescence analyzer. The zero is calibrated followed by the photo-multiplier tube (PMT) and the converters.

The sampling methods used in flux chamber sampling are presented in figure 6.4. The flux chamber was prepared and set in the proper location. The location of the flux chamber was placed randomly with respect to the spatial variables. The zero air flow rate for the chamber was set at 7 L/min. The chamber was allowed to equilibrate for 30 min followed by 30 min of sampling. The sample flowed to the analyzer, where the concentration was measured. The concentration was converted to a flux. Multiple samples were collected at random (spatially) for a particular source. The emission rate for the source was determined from the multiple samples.

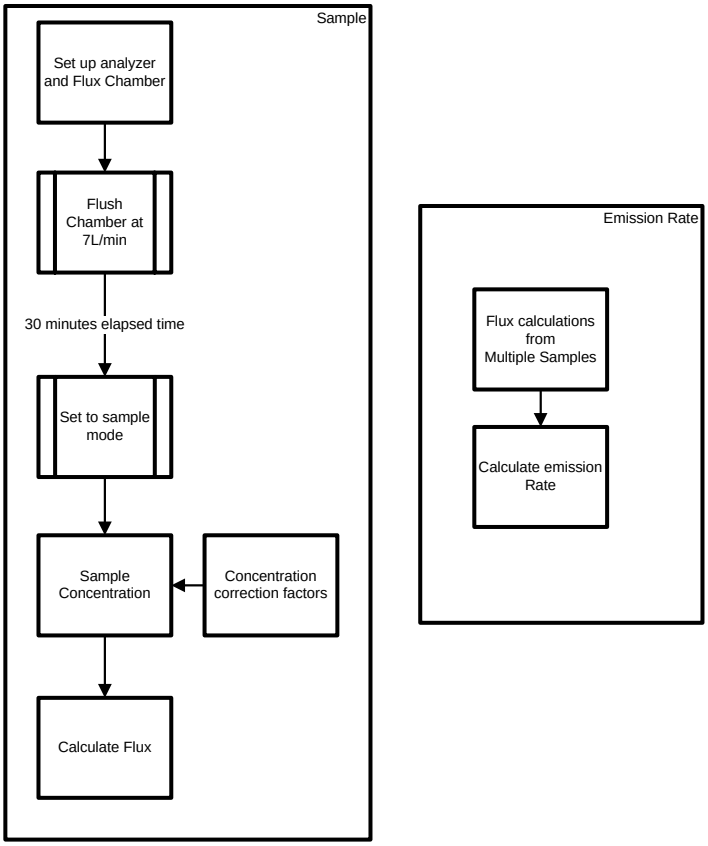


Figure 6.4. Flux chamber sampling method. Zero air enters the chamber at 7 L/min. The flux is calculated from the concentration and flowrate. The emission rate is calculated from multiple flux measurement for a given area.

The emission flux was calculated using equation 6.12.

$$E_{fl} = \frac{QC_v MW}{1467 A_{ch}} \tag{6.12}$$

where:

E_{fl} = emission flux [$\mu g/m^2/s$]

Q = flow of zero air into chamber [sL/min]; STP: 25°C, 1 ATM

A_{fc}= Area of flux chamber (footprint) [m^2]

C_v = volumetric concentration of ammonia [ppm_{NH3}]

MW= molecular weight [g/mol]

The average emission rate of the source was found by finding the expected value of a statistical distribution that best fits the distribution of emission fluxes of a source and multiplying the area of the source.

Identifying sources of Uncertainty

In identifying sources of uncertainty, each process was examined to determine components that contribute to the overall uncertainty. During calibration several components contributed to the uncertainty including the analyzer, flow meters, calibration standard, zero air, and data logging equipment (figure 6.2 and 6.3). For sampling, the calibrated analyzer, data logging equipment, flow meter and flux chamber dimensions contributed to the flux uncertainty. A cause and effect diagram showing the relevant uncertainty sources is presented in figure 6.5.

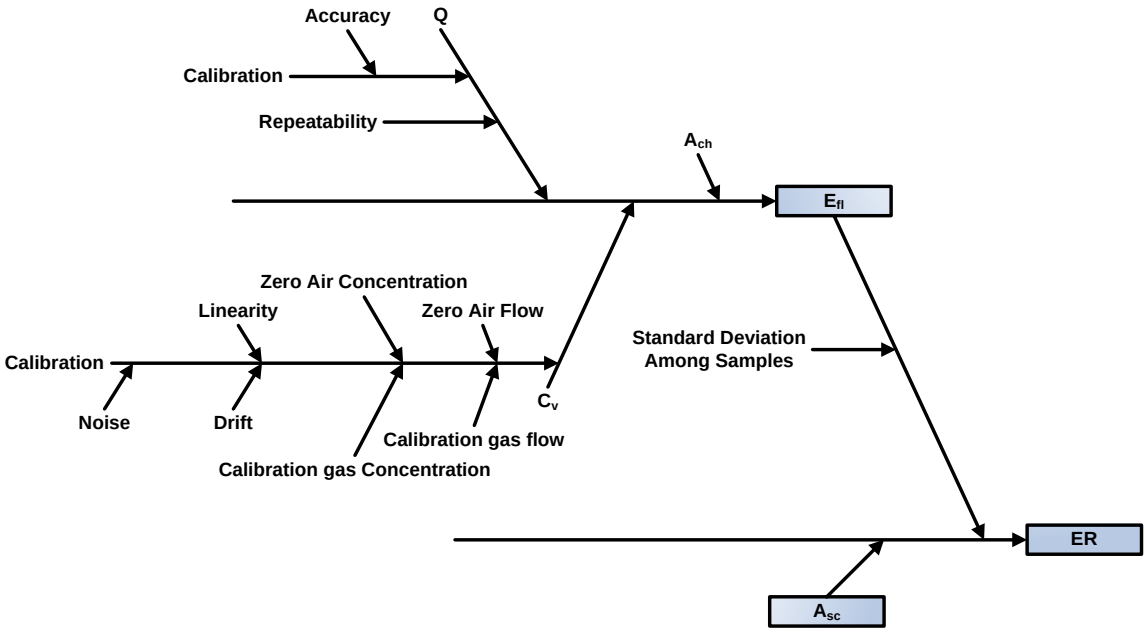


Figure 6.5. Uncertainty cause and effect diagram. Emission rate uncertainty is caused by uncertainties due to area measurement, emission flux, and sample standard deviation. Emission flux uncertainty is caused by uncertainties in concentration measurement, flowrate measurement, and area measurement of the chamber.

ER= Emission rate, [kg/day]

A_{sc}=Source area, [m^2]

The uncertainty because of instrumentation for the system was generated from three major components: the analyzer, analog inputs and outputs, and flow meters. Each component's data sheet contained the necessary information to estimate the instrument uncertainty. Table 6.1 shows the uncertainty levels for each of the components.

Table 6.1. Uncertainty levels for instrumentation

Manufacturer	Component	Model	Uncertainty type	Reported uncertainty	Uncertainty distribution	Standard Uncertainty	Notes
National Instruments	Field point module	FP-AO-210	Gain	0.40%	normal	0.20%	a
			Offset	14mV	normal	7mV	
Aalborg	Mass flow controller	GFC-17	Accuracy	1.5% FS	normal	0.25% FS	b
			Repeatability	0.5% FS	normal	0.75% FS	
Thermo	Ammonia analyzer	17C	Linearity	1% FS	normal	0.5% FS	c
			Span drift	1%FS	normal	0.5% FS	
			Zero drift	1 ppb	normal	0.5 ppb	
			Zero noise	0.5 ppb	normal	0.25 ppb	
Praxair	Calibration Gas	50 ppm NH_3	Accuracy	2%	rectangular	0.58 ppm	
		50 ppm NO	Accuracy	2%	rectangular	0.58 ppm	
		50 ppm NO_2	Accuracy	2%	rectangular	0.58 ppm	
	gps		Accuracy	5m	normal	2.5m	

a. (National Instruments, 2004b)
b. (Aalborg, 2002)
c. (Thermo, 2002)

The uncertainty of the ammonia analyzer presented in Table 6.1 is the uncertainty of the sensor. Since the analyzer multiplexes to obtain the NH_3 and NO_2 readings by difference, the total uncertainty must be taken into account. Each instrumentation uncertainty was assumed to be normally distributed while uncertainty of the calibration gas was considered rectangular. This was because of the type of analysis performed by the manufacturer.

Calculating the combined uncertainty

Uncertainty analysis of the analyzer and flow meters were performed using the law of propagation of uncertainty (type B analysis). The law of propagation of uncertainty is based upon the first order Taylor series approximation of the measurand

'y' as determined to be a function of 'n' other quantities (Taylor and Kuyatt, 1994). The law of propagation of uncertainty allows individual standard uncertainties to be collected to determine the combined standard uncertainty of the system. Equation 6.13 shows how the combined standard uncertainty is obtained. All uncertainties placed in equation 6.13 must be standard uncertainties, expressed as the standard deviation (Eurachem/CITAC, 2000).

$$u_c(y(x_1, x_2, ...)) = \sqrt{\sum_{i=1}^{n} c_i^2 u(x_i)^2} \tag{6.13}$$

where:

u_c = combined uncertainty

$y(x_1, x_2, \ldots)$ = function with several input variables x_n

c_i= sensitivity coefficient

$u(x_i)$ = uncertainty of input variable

The sensitivity coefficient is obtained by evaluating the partial differential of y with respect to x_i as shown in equation 6.14.

$$c_i = \frac{\delta y}{\delta x_i} \tag{6.14}$$

By using a first order Taylor series, each error term was assumed to be independent. This was likely not true in the analyzer. Thus the first order Taylor series over estimates the uncertainty. By examining the process structure of the analyzer, the zero drift, span drift, and linearity for NO, NO_x and N_t were found to be closely related. This is because the same sensor is used to measure each of the concentrations. The uncertainties of zero drift and span drift are long-term (1 day) uncertainties that act as a bias in the short-term (1 min) time scale. The linearity of the sensor is the distance the true value lies from a straight line approximation of the measured value. When the NO, NO_x, and N_t readings were very close, the linearity of the sensor acted as a bias. The linearity term became negligible near values of zero. However, when the concentrations

of each were not close to each other or zero, the linearity needed to be considered in an uncertainty analysis.

Type A uncertainty

Type A uncertainties were involved in calibration curves and the sample distribution. Calibration curves were fitted using linear regression. The uncertainty for each regression coefficient was equal to the standard error of the respective coefficient. Multiple flux samples were taken during a sampling period. The flux samples varied because of spatial and time variation. The total variation from the time and spatial variables was assumed to follow a distribution. The sample distribution was found by fitting a cumulative density function (CDF) of a statistical distribution to the CDF of the data. The parameters were estimated for the distribution by non linear regression and the standard error for each coefficient was used to estimate uncertainty about the expected value of the distribution.

Results

The analyzer was calibrated using 49.3 ppm NO, 49.9 ppm NO_2, and 49.7 ppm NH_3 standards. The standards were diluted with zero air to produce calibrations at 0, 4, 8, 12, and 16 ppm set points. The analyzer was set to a 300-s averaging time and a full scale range for each gas was set to 20 ppm. The results of the uncertainty analysis attributed to calibration are presented in table 6.2. The table presents the uncertainty of the instrument based on a 20 ppm full scale setting. The analyzer has approximately a 2.77% standard uncertainty when measuring 16 ppm with a 20 ppm full scale setting.

Table 6.2. Instrument uncertainty for 20 ppm full scale range. The uncertainty value remains nearly constant throughout the entire range. At low concentrations, the percent uncertainty becomes large.

Concentration	Uncertainty	
ppb	Percent of reading	ppb
500	99.80%	499
1000	49.50%	495
2000	24.30%	486
4000	11.78%	471
6000	7.63%	458
8000	5.61%	449
10000	4.42%	442
12000	3.66%	439
14000	3.14%	439
16000	2.77%	443
18000	2.49%	449

Application of uncertainty to field data

Unpublished concentration data from an open lot dairy in central Texas was used to estimate the emission rate. Seventy two samples were obtained from two open lots at random. Flux chambers were placed at random intervals in the open lots. Management practices from each lot were identical. Sample concentrations were plotted in a histogram as shown in figure 6.6.

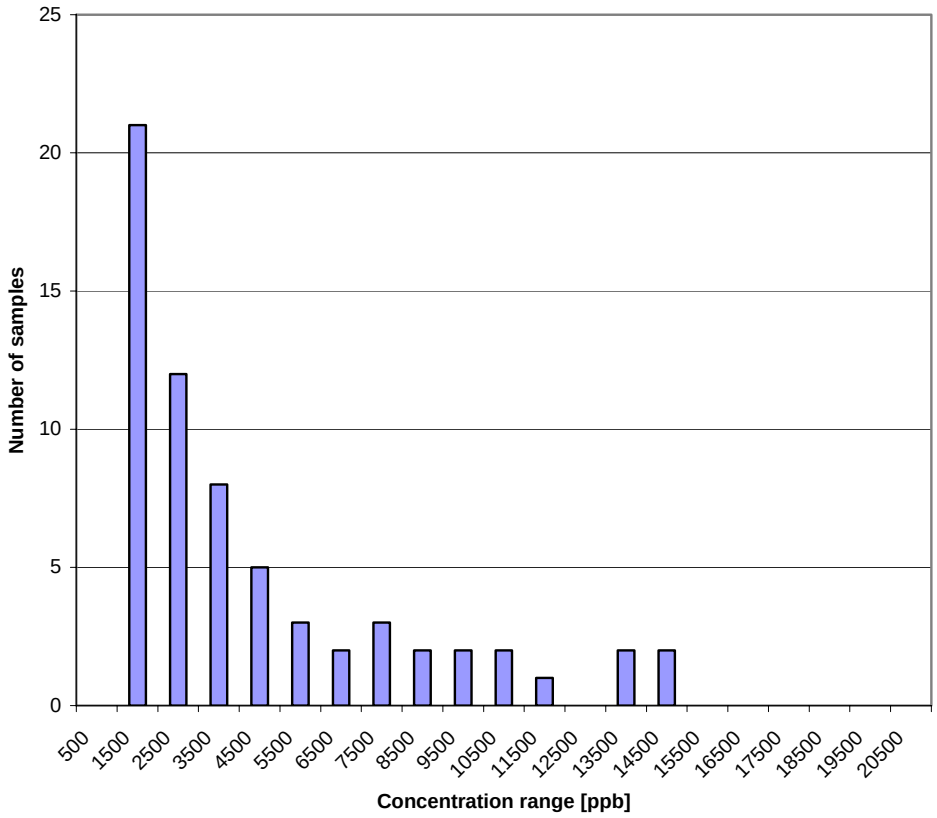


Figure 6.6. Histogram of concentrations of ammonia samples taken from open lots.

SPSS 11.5 (SPSS, Chicago, IL) was used to fit the lognormal distribution by nonlinear regression. The data was found to fit with an expected value of 3 ppm and geometric standard deviation (gsd) of 3.4. The cumulative density function (CDF) with the flux data is presented in figure 6.7. The standard error of the mean was found to be 32 ppb. A total of 72 data points are represented in the CDF. The lognormal distribution fits well with this dataset.

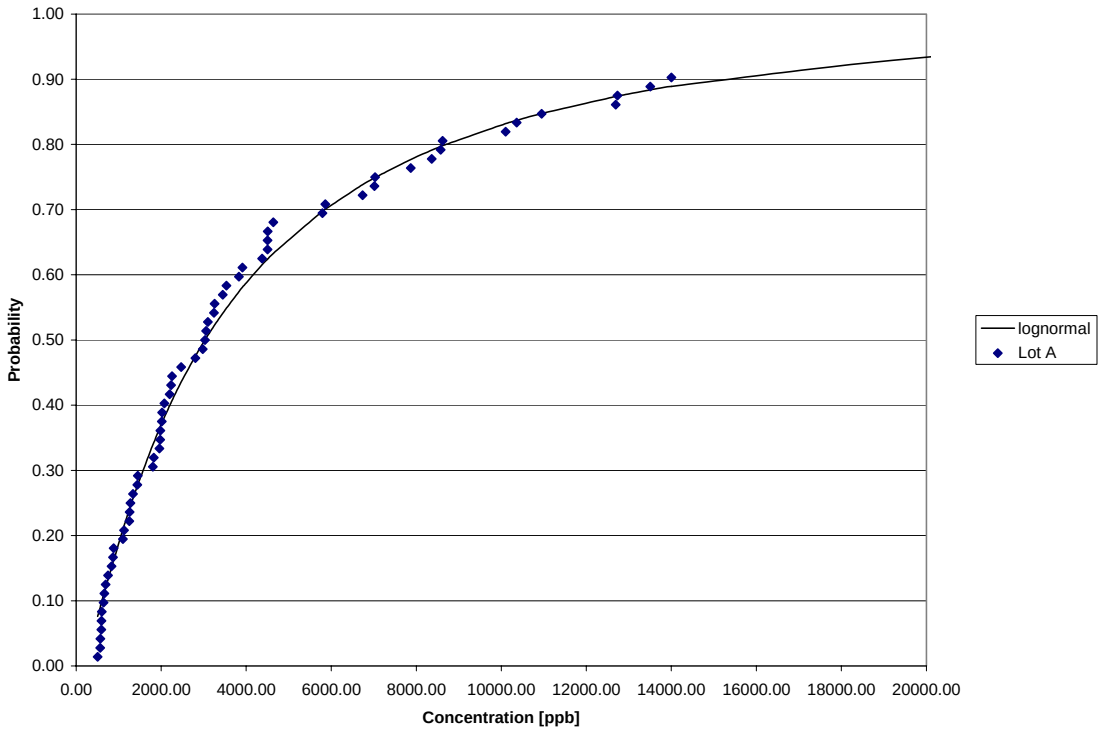


Figure 6.7. Cumulative density function for ammonia samples taken from dairy open lot on July 2004.

Uncertainties of the average emission rate and emission flux were calculated using the first order Taylor series. The flush rate for the flux chamber was 7 L/min (standard conditions: 25°C and 1 atm). The total area for the dry lots measured in this study was approximately 17000 m^2. For this particular set of data, the standard uncertainty of the emission rate was found to be 17%. Much of the uncertainty for the emission rate was found to originate from the analyzer and its calibration. One method to reduce uncertainty of the analyzer is to select a smaller analyzer range. However, nearly 10% of the samples were invalidated because the concentration exceeded the selected instrument range of 20 ppm. Because of the range of the data, a smaller analyzer range could not be used to reduce the uncertainty.

Uncertainties play an important role also if the instrument is used for ambient sampling. Assuming the background ambient concentration of ammonia for a feed yard is between 0 ppb and 500 ppb and the downwind concentration is between the

background concentration and 2000 ppb. Upwind and downwind analyzers would be calibrated for 2000 ppb. Assuming the average upwind concentration is 100 ppb and the average downwind concentration is 600 ppb, the contribution of the source is 500 ± 67 ppb (1 SD). This results in a standard uncertainty of 13.5% in the concentration measurement. The concentration is only one component of the entire uncertainty budget for ambient samplers. Other factors of uncertainty, such as, meteorological conditions and modeling uncertainty play a significant role in determining an emission rate.

Conclusion

An essential item in an engineer or scientist's toolbox is uncertainty analysis, which allows a confidence interval to be placed around the results of a study. When information is transferred to the scientific community, confidence intervals allow the reader to assess the quality of data taken and the statistical significance of compared values. In air pollution engineering, results of a study are often used to make policy decisions. Reporting the uncertainty with the results allows the policymakers to make sound decisions regarding emissions. The proper ranges must be used with the instrumentation to ensure a reasonable uncertainty. It is often difficult to determine the average and variability of concentration data in order to select the proper ranges. Results from this study suggest a calibration standard uncertainty of 2.77% at a concentration of 16 ppm on a 20 ppm span. This uncertainty represents the range obtained using a first order Taylor series. An emission rate for an open lot dairy with stocking density of approximately 50 m^2/hd was found to be 5.41±1.47 kg/1000hd/day (1 SD) in July 2004 using the method described. This emission rate should not be used as an emission factor because emissions vary widely with management practices and meteorological conditions. This emission rate represents only one of the processes in a facility.

CHAPTER VII

PERFORMANCE OF THE SYSTEM: SYSTEM RESPONSE ANALYSIS

Ammonia and hydrogen sulfide are two odorants that result from biological breakdown of manure from animal feeding operations. Ammonia is produced primarily from the breakdown of urine while hydrogen sulfide is a result of anaerobic breakdown of waste in a lagoon. Many methods exist for measuring ammonia and hydrogen sulfide. The chemiluminescence ammonia analyzer (Thermo Electron Corp. 17C, Franklin, MA) is one method used for measuring ammonia concentrations and the pulsed florescence analyzer (Thermo Electron Corp. 450C, Franklin, MA) is a method used to measure hydrogen sulfide concentrations. Understanding the dynamic response of a measurement system is necessary when measuring a dynamic emission rate or performing tests that involve a dynamic concentration.

Product datasheets often contain data regarding the dynamic response of the specific component. Using the information provided on each datasheet, the entire system response can be found. The datasheet however, may not provide a complete look at a specific complex component such as an analyzer. Different settings of the analyzer averaging times will provide different response times.

The goal of this study is to describe the specific responses of the ammonia and hydrogen sulfide analyzers to a concentration input. A transfer function was used to describe the system response using available mathematical transforms. Transfer functions for tubing connecting the analyzers was assessed using nitric oxide (NO) as the transport gas. A transfer function was determined as a function of tubing length.

Background

Finding a transfer function involves measuring the response of the specific instrument or component to a stimulus signal. The stimulus signal may take any form, but a sine wave, square wave (step function), or impulse function are most easily

interpreted. Depending on the system involved, different stimulus signals are better suited to finding the response. For example, a first order system that is very slow may not show a response to an impulse function but would be better measured by a low frequency square wave.

Two transforms that control engineers often use are the Laplace transform and the Z-transform. The Laplace transform is used to identify systems on a continuous time basis. The Z-transform is used on discrete time systems. These transforms allow for easier system analysis. One of the properties of the transform is the ability to measure each components system response separately and combine the results by superposition to form the entire system response. This can be done by a multiplication of the individual transfer functions.

Two common signal responses found in signal processing are the first order response, and the transport delay. The first order response is the response characterized by a continuously stirred tank reactor (CSTR) (Perry & Green, 1997). The transport delay is often characterized by a plug flow reactor (PFR) (Perry & Green, 1997). These responses to a step function are presented in table 7.1.

Table 7.1. Step responses and transforms to common signal responses. (Franklin et al., 2002)

Signal Response Type	Step Response (time domain)	Laplace Transform	Z-Transform
1^{st} order	$G(t) = 1 - e^{-at}$	$\frac{a}{s+a}$	$\frac{z}{z - e^{aT}}$
Transport delay	$G(t) = G(t - T_d)$	$G(s) = e^{-T_d s}$	z^{-k_0}

When accounting for plug flow in a long tube with a compressible fluid, the density of the fluid must be taken into account. The time delay may be found by using the following equation:

$$T_d = \frac{A_{cs} L^2}{\dot{M} \int_0^L \frac{1}{\rho(x)} dx} \tag{7.1}$$

where:

T_d = time delay [s]

A_{cs} = cross sectional area of tube [cm^2]

L = length [cm]

$\dot{M}$ = mass flow rate [g/s]

$\rho(x)$ = density as a function of length [g/cm^3]

The density of the fluid may be found using the Peng-Robinson Equation of state (Perry & Green, 1997). The equation corrects for non-ideal gas conditions that occur at high pressure.

Several tools are available for measuring the system response of a component. One tool used for identifying the system response is the System Identification Toolkit of LabVIEW 7.1 (National Instruments, Austin, TX). The toolkit is able to input a stimulus and response signal and return the transfer function of the system response.

A signal is made up of two components, the deterministic portion and the stochastic portion. The stochastic portion of the signal results from uncertainty of the system. The deterministic portion is the system response. Depending on the origin of the stochastic portion of the signal, different models may be used to identify the system. The general linear model as described in the System Identification Toolkit User Manual (National Instruments, 2004b) may be described as in figure 7.1.

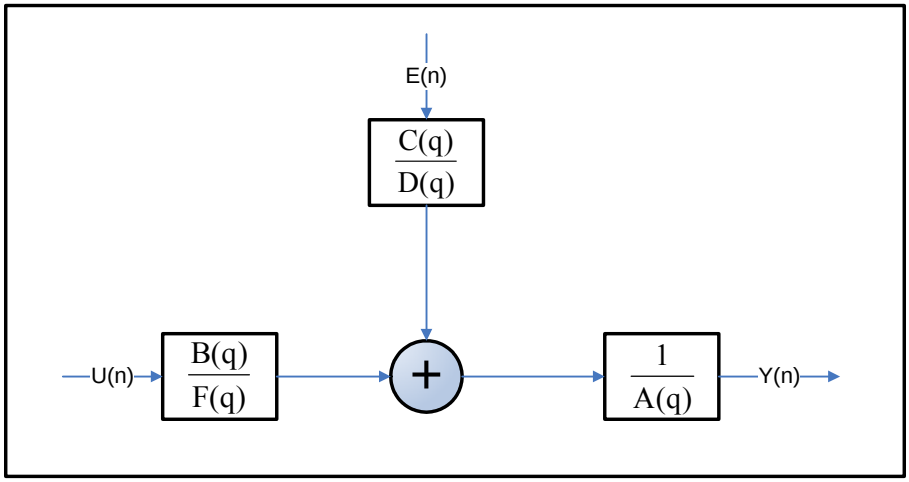


Figure 7.1. Signal flow of general linear model. U(n) and Y(n) are the inputs and outputs of the respective system. E(n) is the stochastic noise of the system. A(q), B(q), C(q), D(q), and F(q) are polynomials that make up the transfer function where q is a frequency domain variable.

By assuming that C(q), D(q), and A(q) are equal to one, the model reduces to the output error model as shown in figure 7.2. This model assumes the stochastic portion of the model strictly affects only the output. This assumption holds true when the original signal contains very little noise. A measured signal may be represented by the mean (deterministic) and coefficient of variation (CV, stochastic) of the signal. The quality of the signal is often described by the signal to noise ratio, where the signal to noise ratio is defined as 1/CV for a measured signal (Smith, 1999).

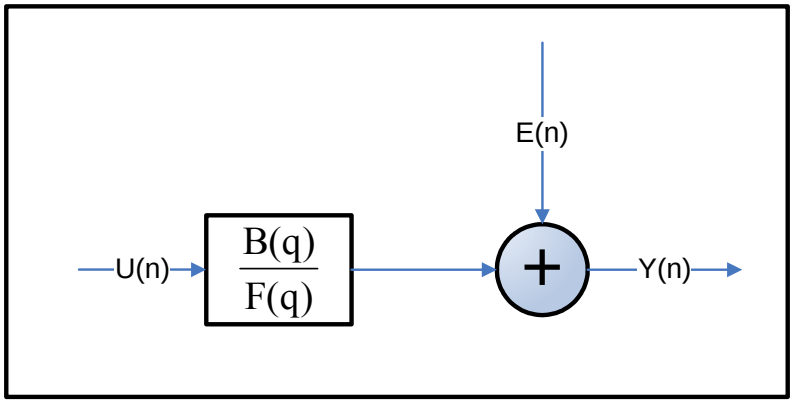


Figure 7.2. Output error model. In the output error model, A(q), C(q), and D(q) are assumed to be one. The stochastic portion of the signal only affects the output.

To understand the signal response of the analyzers, important parameters that may affect the response of the analyzer must be understood. The NH_3 chemiluminescence analyzer and H_2S pulsed fluorescence analyzer may be set for one of several modes and one of several averaging times. The NH_3 analyzer may be set up in manual mode to measure nitric oxide (NO), nitrogen oxides (NO_x), or nitrogen compounds (N_t). In the manual mode, the averaging times range from 1s to 300 s (Thermo, 2002a). In automatic mode the analyzer multiplexes each of the manual modes in order measure NH_3 and nitrogen dioxide (NO_2). In automatic mode, the analyzer averaging times may range from 10 s to 300 s (Thermo, 2002a). The H_2S analyzer likewise may be set up for automatic and manual modes. In manual mode, the combined sulfur (cS) or sulfur dioxide (SO_2) may be measured with an averaging time range of 10 s to 300 s (Thermo, 2002b). In auto mode, the H_2S, cS, and SO_2 may be measured with averaging times ranging from 60 s to 300 s (Thermo, 2002b). The analyzer system response may be obtained if the analyzers contain the zero/span/sample valve option.

Materials and Methods

The experimental apparatus is shown in figure 7.3 with flowrate set points for each component. The laboratory setup consisted of one analyzer, three mass flow controllers (GFC17, Aalborg, Orangeburg, NY), zero air generator (737-12A, Aadco Instruments, Inc., Village of Cleves, OH), and PFA grade 3.2 mm (1/8 in.) inside diameter tubing. Several solenoid valves (Gold Ring Series 20, Parker Hannifin Corp., Madison, MS) were used to control flow to specific components.

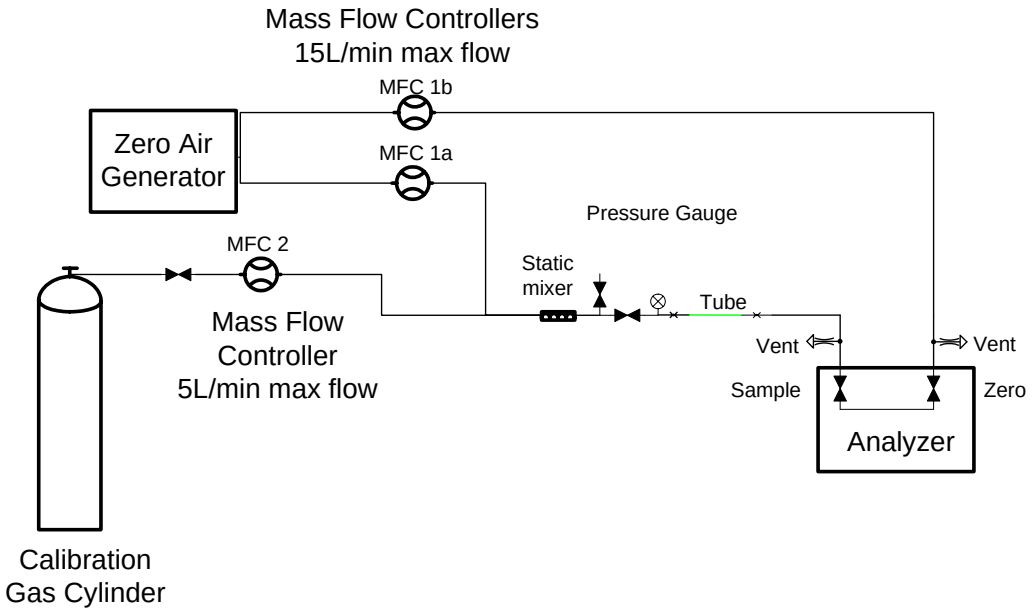


Figure 7.3. Laboratory apparatus for determination of system response. The apparatus contains a gas dilution system for precise mixing of calibration gases. The apparatus may be used to determine analyzer system response and tubing system response.

System response was measured for the analyzers by performing the following steps:

- *Calibrate the instruments*- the instruments were calibrated using the appropriate calibration gas according to manufacturer's guidelines. Ultra High Purity gases were mixed with at least 25% purified air.
- *Measure the system response*- The system response was measured by switching the analyzer zero/span/sample valve option. The sample stream into the analyzer was set so that a specific concentration of calibration gas was allowed to vent. At the same time purified air was sent to the zero stream of the analyzer. The analyzer was switched from the zero stream to the sample stream. The response to the switch was logged on a one second interval using LabVIEW software communicating via the RS232 port. Data was saved for further analysis in a spreadsheet file. The system response for the NH_3 analyzer was measured for N_t manual mode for two concentration of NO (20 and 40 ppm) and five concentrations of NH_3 (2.5, 5, 10, 20, and 40 ppm). The system response was measured in auto mode with 40 ppm NO, 40

ppm NH_3, and 2.5 ppm NH_3. The averaging times for the NH_3 analyzer were set to 1s in manual mode and 10 s in auto mode. The H_2S analyzer was measured for cS manual mode and auto mode with 4 ppm H_2S and 4 ppm SO_2. The averaging times for the H_2S analyzer were set to 10 s in manual mode and 60 s in auto mode. The resulting system response is the response to a step function.

- *Analyze system response*- System response is analyzed by first noting and removing the transport delay from the data. A Z-transform is applied to the data using the LabVIEW System Identification Toolkit. The discrete transfer function is converted to a continuous transfer function by using the forward algorithm to calculate the Laplace transform. The forward algorithm is shown below as

$$Z \to 1 + sT \tag{7.2}$$

System response to the tube was performed by using the NH_3 analyzer set to N_t mode with an averaging time of 1s. The following steps were performed to determine the system response to tubing.

- *Calibrate the instruments*-Single point calibration is performed according to manufacturers specifications at the given concentration used to determine tubing response.
- *Measure the system response*- The system response was measured with 6 lengths of tubing (36.6m, 82.3m, 128.0m, 173.7m, 219.5m, 265.2m) for 20 ppm of NO and two flowrates (4 and 7 L/min). The system response included both the analyzer response and the response of the tubing to a step function.
- *Analyze system response*- System response was analyzed by first noting and removing the transport delay from the data. The transfer function of the analyzer was used to separate the response of the analyzer and tubing. A Z-transform was applied to the data using the LabVIEW System Identification Toolkit. The discrete transfer function was converted to a continuous transfer function by using the forward algorithm to calculate the Laplace transform.

Results and Discussion

The NH_3 analyzer system responses are presented in Table 7.2.

Table 7.2. System responses of NH3 analyzer to step inputs of different magnitude

Mode	Input	Transfer function	Delay [s]
Manual N_t (1s averaging time)	NO	$\frac{0.95e^{-3s}}{s+0.95}$	3
	NH_3	$\frac{(s+1)(s+0.053)e^{-3s}}{(s+0.43)(s+1.02)(s+0.045)}$	3
Auto (10 s averaging time)	NO & NH_3	$\frac{0.097e^{T_d s}}{s+0.097}$	<30

In N_t mode, the transfer function was a function of the gas being input into the analyzer. One reason for this was that ammonia must be converted to NO before being measured. The transfer function took into account the adsorption and conversion of ammonia. Although the reaction rate was fast, the reaction does add to the system response. In Auto mode, the responses were essentially the same but the delays were dependent on when the analyzer switched modes. The response when in the auto mode was much slower than that of the manual N_t mode.

Table 7.3. System responses of H_2S analyzer for various inputs

Mode	Input	Transfer function (including delay)	Delay
Manual cS (10s averaging time)	4 ppm (SO_2 & H_2S)	$\frac{0.074e^{-T_d s}}{0.074+s}$	<10
Auto (60 s averaging time)	4 ppm (SO_2 & H_2S)	$\frac{0.064e^{-T_d s}}{0.064+s}$	<100

In manual mode the H_2S and SO_2 had essentially the same response times. In the auto mode, the responses were much slower than in the manual mode. The responses for the two gases in auto mode were almost identical.

The transfer function for the tubing is shown in equation 7.3

$$\frac{0.95e^{-T_d s}}{0.95+s} \tag{7.3}$$

where the time delay, T_d is a function of the length of tube. Figure 7.4 shows the measured and modeled time delay. The delay was found to follow equation 7.1 closely. The first order portion of the transfer function shows that some dispersion occurs in the tubing.

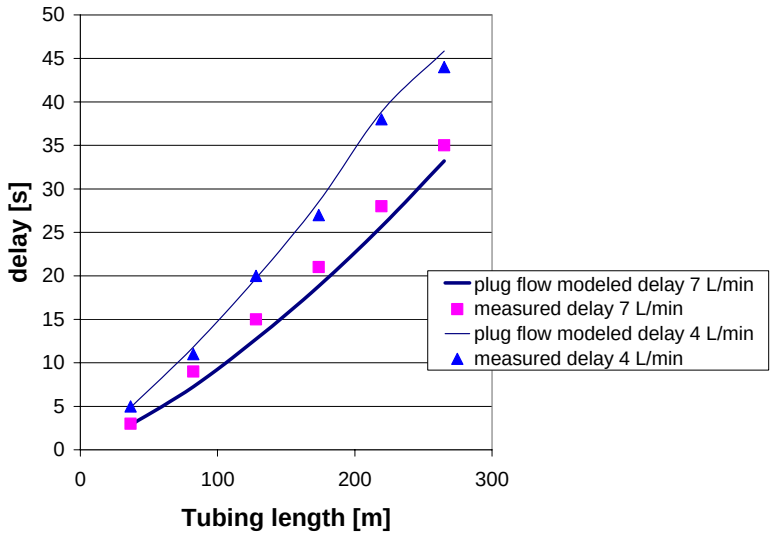


Figure 7.4. A plug flow reactor transfer function was found to model the time delay in the tubing.

When using the NH_3 and H_2S analyzers with a flux chamber, the response is much faster than the chamber response. This can be shown by applying the first order model of the chamber ash shown in equation 7.4.

$$C(t) = (C_f - C_i)(1 - \exp(-t/\tau)) + C_i \qquad (7.4)$$

where $\tau = V/Q$ in the above equation. The time constant, τ, is considered the response time of the chamber. For 7 L/min and a 65 L chamber, the theoretical response time is 9.28 minutes for the chamber. Because of this long response time, correction for the analyzer response is not necessary. However, when measuring NH_3 and H_2S at a source without the use of the flux chamber, the response must be taken into account. The analyzer showed a delayed response that is first order in auto mode. The importance of obtaining accurate data from a dynamically responding source increases when multiple sample streams are multiplexed. The tubing that connects the sample port and the analyzer not only effects the sample time but may have a significant response due to adsorption of ammonia if a long length of tube connected the sampling head and analyzer. This study did not measure the adsorption kinetics response to tubing.

Adsorption kinetics on polymer tubing increases the amount of air that must be sampled before a measured result accurately depicts an actual concentration sampled.

Conclusion

Several conclusions can be drawn from the work presented:

- The transfer function for the 17C was a function of the gas input. The transfer function was slower for ammonia than for nitric oxide since ammonia must be converted to nitric oxide before being measured in the analyzer.
- In auto mode, the analyzer response is much slower than in the manual mode. This was primarily because of the averaging time used was smaller in the manual mode.
- The transfer function for the tubing was found to follow a first order response with delay. The delay transfer function was found to follow the modeled time delay for a compressible fluid.

Understanding system response for air quality measurement systems is important when measuring dynamic systems. The system response must be taken into account so that accurate results may be obtained from dynamically changing measurements.

CHAPTER VIII

ADSORPTION KINETICS OF AMMONIA ON FLUX CHAMBERS

Ammonia from animal feeding operations is emitted as a result of biological breakdown of animal waste. Confined animal feeding operations have come under scrutiny by environmental interest groups, the U.S. Environmental Protection Agency (EPA), and nearby residents. Ammonia is one of many odorants that contributes to the odor emissions from an animal feeding operation. Ammonia is known to have a pungent odor and may cause respiratory diseases in both animals and humans if breathed in large quantities. Particulate matter may form from ammonia by reacting with nitrogen oxides (NO_x) and sulfur oxides (SO_x) in the atmosphere causing further respiratory damage.

One method for measuring ammonia emissions from a surface is a flux chamber. A flux chamber measures the potential for a surface to emit a certain pollutant. The sampling protocol for a flux chamber is detailed in Eklund (1992), Gholson, et al. (1989), and Kienbusch(1986). Since the chamber isolates the surface from its natural environment, interferences may bias a measurement. One of the interferences of the flux chamber that affects the measurement of ammonia is adsorption. The focus of this study was to determine the kinetics of adsorption when the chamber was exposed to different concentrations of ammonia. The laboratory study focused on determining whether adsorption of ammonia on the chamber walls was significant.

The method used in sampling with a chamber involved flushing the chamber with a set flowrate while continuously sampling the headspace. The chamber was allowed to vent during the test. Studies done by Kienbusch (1986) indicated that the chamber acts as a continuously stirred tank reactor (CSTR) when used in this manner. One of the characteristic properties of a CSTR is a first order response to a step change in input. Thus, for a step function input of concentration, a chamber without interferences will have an output concentration that will be described by the first order equation:

$$C(t) = (C_f - C_i)(1 - \exp(-t/\tau)) + C_i \quad (8.1)$$

where $\tau = V/Q$. In the above equation, C(t) is the concentration at time t, C_f is the final concentration, C_i is the initial concentration, V is the volume of the chamber, and Q is the actual flow rate into the chamber. The flux chamber method assumes that the concentration leaving the chamber and the concentration in the chamber are equal, that is, the flux chamber acts as a well mixed reactor.

Adsorption involves ammonia molecules accumulating at the surface of the chamber. Physical adsorption is a result of van der Waals interactions between the surface and solute molecules (Perry and Green, 1997). Chemical adsorption results in a breakdown of a solid over time as a result of exposure to a gas (Perry and Green, 1997). Materials exhibit different adsorption potentials. Materials used in an ammonia measurement system are generally selected to have a low adsorption potential for ammonia and other chemicals often found when measuring the ammonia.

Adsorption isotherms describe the adsorption equilibrium behavior of a surface. Adsorption isotherms relate gas adsorption dependence to the gas partial pressure at a constant temperature. Several isotherms have been used to describe adsorption including: the Langmuir isotherm; Brunauer, Emmett, and Teller (BET) isotherm; and Freundlich isotherm. The Langmuir isotherm is used to describe monolayer adsorption on a homogeneous surface. The Langmuir isotherm is based upon the assumptions that all adsorption sites are equivalent, no horizontal interactions exist among adsorbed molecules, and the heat of adsorption is the same for all molecules to any site (Seinfeld and Pandis, 1998). The Langmuir isotherm may be described by:

$$n_i = \frac{n_i^s k_i p_i}{1 + p_i k_i} \quad (8.2)$$

where n_i^s is the adsorption capacity (mass), k_i is an isotherm parameter (1/partial pressure), n_i is the mass adsorbed (mass), and p_i is the partial pressure of the solute.

The BET isotherm may be used to describe multilayer adsorption on a homogeneous surface. The BET isotherm is an extension of the Langmuir isotherm with the additional assumptions that each adsorbed molecule provides a site for an additional layer and the heat of adsorption for each additional layer after the first is equal to the latent heat of evaporation for the bulk condensed gas (Seinfeld and Pandis, 1998). The Freundlic isotherm may be used to describe adsorption for a heterogeneous flat surface. The isotherm assumes an exponential distribution of heats of adsorption (Perry and Green, 1997). The Freundlic isotherm lacks the required linear behavior in the Henry's law region. Because of the low coverages resulting from low concentrations typical in ammonia measurement, the Langmuir isotherm may be used to describe the adsorption characteristics.

Isotherms only describe the equilibrium behavior of adsorption. To understand adsorption in chamber, the kinetics of adsorption must be used. Kinetic theories that describe Langmuirian adsorption are often used in situations in which the solute is dilute. The Theory of Activated Adsorption, Absolute Rate Theory, the Elovich equation, and the Statistical Rate Theory (SRT) are four methods that describe Langmuirian adsorption. The Theory of Activated Adsorption contains parameters that are difficult to independently measure (Ward and Findlay, 1982). One other problem of the Theory of Activated Adsorption is that it predicts a linear function of coverage when the adsorption rate is actually highly nonlinear in the initial low coverage portion (Ward and Findlay, 1982).

The Absolute Rate Theory was suggested by Clark (1970) to elucidate discrepancies that occur when a surface is initially exposed to a gas (Ward and Findlay, 1982). With the Absolute Rate Theory, explicit functions for the surface coverage of adsorption and desorption cannot be found (Rudzinski and Panczyk, 2002). Additionally, the expression does not clearly show the dependence of the activation energies of adsorption and desorption on surface coverage (Rudzinski and Panczyk, 2002).

The Elovich equation has been more successful at correlating empirical results. However, the Elovich equation initially under-predicts adsorption and does not contain a factor that limits the amount of adsorption (Ward and Findlay, 1982).

The SRT assumes that single molecular events result in the transport of molecules from one phase to another (Ward et al., 1982). The transition probability is derived using a first order perturbation analysis of the Schröderinger equation (Ward, et al., 1982). The SRT may over predict in instances immediately after a bare surface is exposed to a gas (Ward and Findlay, 1982). In this case, the limiting factor is the collision rate of the gas molecule with the surface. The chamber is likely not to experience this phenomenon because the dynamics associated with the chamber are generally slow. Rudzinski and Panczyk (2002) give an expression for the SRT as shown below:

$$\frac{d\theta}{dt} = \left[K_a p \frac{1-\theta}{\theta} \exp\left(\frac{\varepsilon}{kT}\right) - K_d \frac{1}{p} \frac{\theta}{1-\theta} \exp\left(-\frac{\varepsilon}{kT}\right) \right] \left[1-\theta^{(e)}\right] p^{(e)} \tag{8.3}$$

with

$$K_a = K_{gs} q_0^s \exp\left(\frac{\mu_0^g}{kT}\right) \tag{8.4}$$

and

$$K_d = \frac{K_{gs}}{q_0^s} \exp\left(-\frac{\mu_0^g}{kT}\right) \tag{8.5}$$

In the above equations, θ is the coverage, p is the partial pressure, ε is the activation energy for adsorption/desorption, k is the Boltzmann constant, T is the temperature, K_{gs} is a constant, q_0^s is the partition function of gas molecules, and μ_0^g is the standard chemical potential for perfect gas. For the chamber, the volume of pollutant present in the chamber is much greater that the amount adsorbed in a short period of time. For this to be true, the partial pressure of the gas would not measurable change because of adsorption. When the chamber is initially exposed to the gas, this assumption

does not hold true. For a volume dominated system, Rudzinski and Panczyk (2002), give:

$$\frac{d\theta}{dt} = \left[K_a p^2 \frac{1-\theta}{\theta} \exp\left(\frac{\varepsilon}{kT}\right) - K_d \frac{\theta}{1-\theta} \exp\left(-\frac{\varepsilon}{kT}\right) \right] \left[1-\theta^{(e)}\right] \tag{8.6}$$

The above equation may be simplified to

$$\frac{d\theta}{dt} = K_{gs} \left[p^2 k_i \frac{1-\theta}{\theta} - \frac{1}{k_i} \frac{\theta}{1-\theta} \right] \left[1-\theta^{(e)}\right] \tag{8.7}$$

The above equation must be changed into mass form to be applicable to the flux chamber. By applying the above equation after changing it into mass form, the amount adsorbed may be found as shown in equation 8.

$$\frac{dn}{dt} = K_{gs} \left[p^2 k_i \frac{n_i^s - n}{n} - \frac{1}{k_i} \frac{n}{n_i^s - n} \right] \left[n_i^s - n_i\right] \tag{8.8}$$

The equation may then be fitted to the measured mass adsorbed. Adsorption kinetics has been traditionally measured in a closed system. Because the ammonia measurement instrumentation did not allow the measurement of adsorption using a closed system, the adsorption was measured using an open system. The adsorption may be found by performing a mass balance to the system. The modeled outlet concentration takes into account the system response of the chamber and instrumentation which may be measured separately to determine the entire system response. Equation 9 below shows the mass balance of the chamber

$$\frac{dm}{dt} = \dot{M}_{in} - \dot{M}_{out} - \frac{dn}{dt} \tag{8.9}$$

where dm/dt is the rate of change in mass of the chamber, $\dot{M}_{in}$ and $\dot{M}_{out}$ are the mass flow rates into and out of the chamber respectively, and dn/dt is the adsorption onto the walls of the chamber.

In order to account for system response, transfer functions were found for each component in the system. The method of Laplace transforms and system responses is detailed in *Feedback Control of Dynamic Systems* by Franklin et al. (2002). By using transfer functions instrument responses of each component may be found separately and then combined to form the transfer function of the entire system. Likewise, the single transfer function of a component in the system may be isolated by removing responses of the other components.

The objectives of this study were to determine the system responses of the instrumentation, develop an isotherm model for adsorption, and develop a method for which adsorption may be estimated for a flux chamber.

Materials and Methods

Adsorption was measured for the chamber by calibrating the instrumentation, measuring the system response without the chamber, measuring the system response with the chamber, and using transfer functions to both remove system response and obtain the chamber response function. The adsorption function was found by applying a mass balance on the chamber. Input concentrations of 5, 10, 20, and 50 ppm were studied to determine the effects of adsorption.

In order to measure the adsorption kinetics of the chamber, laboratory tests were performed under a controlled temperature (20±2°C) and pressure (1±0.01 atm). The experimental apparatus is shown in Figure 8.1 with flowrate set points for each component. The laboratory setup consisted of one Thermo model 17C ammonia analyzer (Thermo, Franklin, MA), mass flow controllers (GFC17-15 L/m, Aalborg, Orangeburg, NY), flux chamber, zero air generator (737-12A, Aadco Instruments, Inc., Village of Cleves, OH), and PFA grade 3.2 mm (1/8 in.) inside diameter tubing as shown in figure 8.1. The 17C ammonia analyzer has both an auto and manual mode of operation. In automatic mode, the analyzer can determine the concentrations of ammonia(NH_3), nitric oxide (NO), and nitrogen dioxide (NO_2). In manual mode, the analyzer can be set to measure the total nitrogen without speciation between the NH_3,

NO, or NO_2. Since a specific calibration gas was used, no speciation was required by the analyzer. The analyzer was set up in N_t mode with a 1 s averaging time. This allowed for faster response times of the analyzer. The flux chamber skirting material was 304 grade SS with a diameter of 0.495 m (19.5 in.) and height of 0.241 m (9.5 in.). The flux chamber featured an acrylic dome top and sweep air tubes from Odotech Inc. (Montreal, Quebec, Canada). The volume of the chamber was 65 L. A static mixer (½-80-PFA-12-2, Koflo, Cary, IL) ensured that the calibration gas and zero air were well mixed before being measured. The chamber pressure was measured using a barometric pressure sensor (PTB100A, Vaisala, Inc., Woburn, MA). Temperature was measured using a HOBO model HO8-007-02 with TMC6-HC temp probe (Onset Computer, Pocasset, MA). LabVIEW with Field Point modules (National Instruments, Austin, TX) were used to control the mass flow controllers and to log data flow and pressure data.

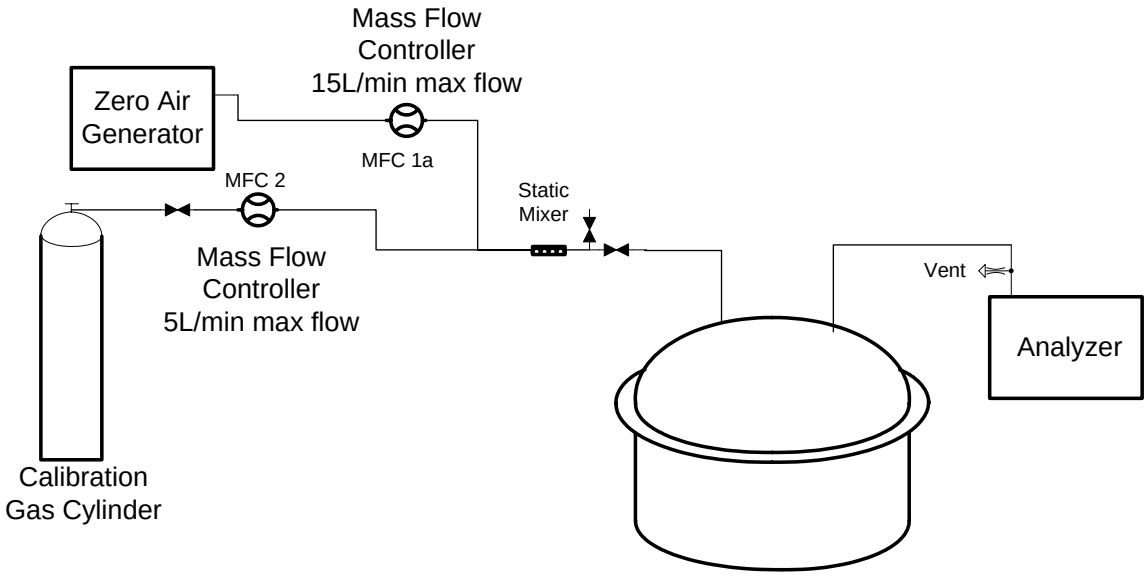


Figure 8.1. Experimental apparatus consisting of mass flow controllers (MFC), flux chamber, calibration gas, and ammonia analyzers (TEI).

Experimental Protocol

The experimental protocol consisted of the following steps:

- Calibration: Calibrations were performed according to the operator's manual of the analyzer. The calibration protocol consisted of zeroing the instrument, then calibrating the sensor with ammonia. The analyzers were calibrated using high purity calibration gases consisting of 100ppm ammonia and 50ppm ammonia (Praxair Inc, Danbury, CT) at the concentration at which the analysis was performed (2.5, 5, 10, 20, and 40 ppm, respectively). Two mass flow controllers were used to mix the calibration gas with purified (zero) air to the correct concentration. The calibration gases were mixed with at least 25% air to ensure sufficient oxygen for oxidation in the NH_3 to NO catalytic converter. Calibrations were performed at the beginning of each day before the test was performed.
- Determine system response: System response was determined by analyzing the output of the instrumentation to a step function with magnitude of the respective concentration measured when determining the chamber response. Transfer functions of each component were determined using Z-transform. The discrete transfer function is converted to a continuous transfer function by using the forward algorithm to calculate the Laplace transform. The forward algorithm is shown below as

$$z \rightarrow 1 + sT \tag{8.10}$$

- Determine chamber response: The chamber response was measured for 5 concentrations of ammonia (2.5, 5, 10, 20, and 40 ppm respectively). The dynamic response was measured for 1 hour for the upward concentration. The system responses of the flow controllers, analyzers, and tubing were much faster than the chamber so they did not need to be removed using transfer functions. The chamber responses were compared to a response to NO. A mass balance

was performed to determine the mass adsorbed. The chamber response was measured for CAAQES chamber 1Y.

- Determine Langmuir parameters: The chamber dynamic response was measured until the system reached steady state conditions to determine the coefficients in the Langmuir isotherm. No measurable mass was adsorbed when the system reached steady state. The mass adsorbed for each concentration was determined by applying a mass balance to the chamber and comparing the actual chamber response to the nitric oxide response. The Langmuir coefficients were determined by fitting the Langmuir equation using nonlinear regression.

Results and Discussion

The chamber was found to follow a first order response for each test and the response was found to be a function of concentration. The change in response was primarily attributed to adsorption of ammonia to the walls of the chamber. Table 8.1 shows the change in the response of ammonia and the resulting mass adsorbed. The time constant for NO in the chamber was much smaller for the given flowrate and size of the chamber. The predicted time constant was 575 [s^{-1}]. The chamber acted as a smaller volume possibly due to incomplete mixing.

Table 8.1. Chamber time constants and mass adsorbed onto chamber for various concentrations of ammonia. The time constants change as a result of adsorption onto the chamber walls.

Concentration [ppm]	Gas	time constant [s^{-1}]	Mass adsorbed [μg]
40	NO	470	*
2.5	NH_3	518	14.7
5	NH_3	508	27.5
10	NH_3	502	46.3
20	NH_3	492	79.8
40	NH_3	485	135.7

* Nitric Oxide was considered a control for the tests

The Langmuir equation was fit to the data using non-linear regression, Levenberg Marquardt algorithm with SPSS 11.5 (SPSS, Chicago, IL). The solution to the regression was then used to find a solution to the Langmuir kinetics equation (equation 8.8). The Langmuir kinetics equation was fit to data collected after 750 s. The Langmuir results are presented in Figure 8.2 and the kinetics results are presented in Figure 8.3.

The Langmuir parameters found are:

Langmuir isotherm $k_i = 0.128$

Langmuir kinetics $k_i = 0.099$

$K_{gs} = 1.9 \times 10^{-4}$

$n^s_i = 395$

Measured $\tau = 441$

Theoretical $\tau = 575$

After 1800 seconds, almost no adsorption occurred. When the chamber is used to measure concentrations in the field, the chamber is allowed to flush for 1800 seconds for a flowrate of 7 L/min. Thus no adsorption occurs while the chamber is being used to measure the concentration if the chamber remains in equilibrium during the sampling portion of the protocol. The adsorption term is a storage term meaning that a specified mass will adsorb for a given temperature and partial pressure. The error in the kinetics equation occurs because of diffusion that must take place in the CSTR. In order for adsorption to occur, the ammonia molecules must come in contact with the surface. Because of the inherent characteristics of the system, measured adsorption is overestimated. The chamber does show to have some incomplete mixing. This provides areas which the chamber provides additional storage.

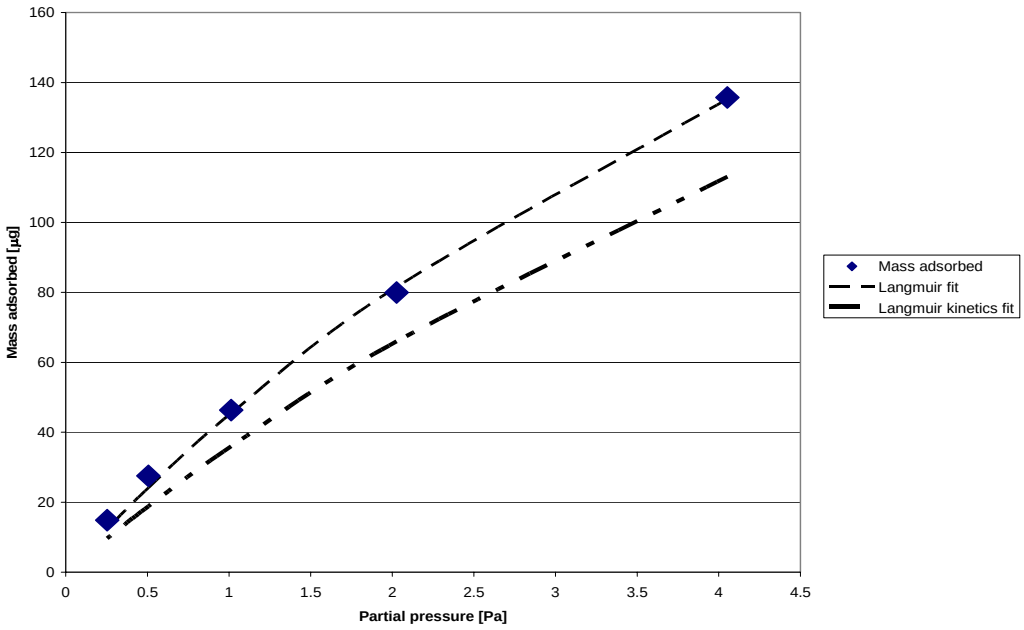


Figure 8.2. Original Langmuir equation fit and Langmuir kinetics fit. The equilibrium mass adsorbed is very small when compared to the total mass of the system.

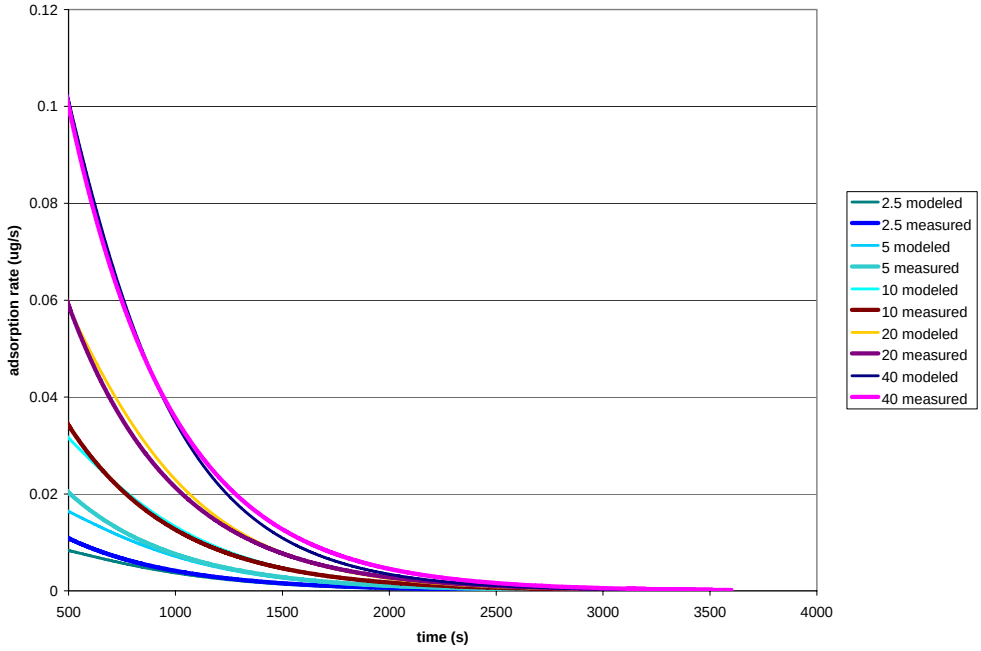


Figure 8.3. Langmuir kinetics fit. After 30 minutes the adsorption rate is very small and does not affect the output concentration.

Conclusions

Several conclusions can be drawn from the work presented.

- The Langmuir method may be used to assess the adsorption of the chamber. The Langmuir kinetics equation for a volume dominated system models the adsorption of the chamber after the initial system response. The kinetic equation for volume dominated systems assumes that there is a significant volume of ammonia such that the concentration is not affected by adsorption. Because of the dynamics of the measurement system, this is true only after approximately one time constant when the inlet concentration change is relatively small.
- The mass adsorbed was relatively small and does not need to be taken into account after a 30 minute flush that takes place before sampling. After 1800 seconds the concentrations were basically unaffected by the adsorption.
- The time constant for the chamber did not match with the theoretical time constant. Further work in this area must be performed to identify why the time constants are different.
- Adsorption does not need to be taken into account for concentrations above 2.5 ppm when used for field measurements.

CHAPTER IX

CONCLUSIONS AND FUTURE RESEARCH

Although ammonia emissions from AFOs are not regulated under the Clean Air Act, they have come under increased scrutiny in recent years. Emission factors have been developed for entire operations without regard to the manure management processes employed for a facility. Because ammonia emissions are closely related to manure management, a science based emission factor must be developed that takes into account manure management practices.

This research focused on the development and performance of a process based ammonia measurement system. The system may be used for analyzing and evaluating BMPs to reduce ammonia emissions from AFOs. The performance evaluation of the system included uncertainty analysis, system response, and adsorption kinetics.

The developed system used a chemiluminescent ammonia analyzer, zero air generator, air compressor, and multiplexer system. A multiplexer system was developed for the system to increase the sampling rate from 0.67 samples per hour to 2 samples per hour. The new multiplexer system allowed for better data retention with improved data handling. The multiplexer was designed to be user-friendly by simplifying the operator interface. The multiplexer system has increased CAAQES productivity in the field by almost 300%. The multiplexer was developed for use with flux chambers, however, it may be used with other methods to sample air pollutants in field or laboratory studies.

The uncertainty for the system was analyzed using the law of propagation of uncertainty. The standard uncertainty of the system was found to be 2.77% when measuring at 80% full scale, but increased to 17% when measuring at 15% full scale. The instrument is not recommended to measure below 15% full scale because the uncertainty quickly becomes more than the measurand. Care must be taken to select the proper range for the instrument to reduce the uncertainty. Knowledge of uncertainty is essential to studies of air pollution. The scientific community must be able to use

uncertainty to access the quality of data presented. Data regarding emissions must be reported with uncertainties so that sound decisions regarding policy may be made.

System responses must be taken into account to measure accurate results from dynamically changing emissions. System responses of the system were measured. Transfer functions were found for the instrument. The ammonia analyzer transfer function was found to be a function of gas of the gas input and averaging time. The tubing transfer function performed as first order system with time delay. The time delay follows the plug flow model for compressible fluids.

The adsorption kinetics of ammonia on flux chambers was measured and found to follow Langmuir kinetics. Adsorption was found to be insignificant after 30 minutes for concentrations above 2.5 ppm at 25°C. The adsorption was found to be a finite storage term for a given concentration. When used with the flux chamber, adsorption does not need to be taken into account for concentrations above 2.5 ppm.

The system design has improved sampling of ammonia at AFOs. The performance of the system was found to be acceptable. The standard uncertainty was found to be less than 20% when measuring greater than 15% full scale. Instrument responses were found to be much faster then the chamber responses for the 10s and 60s averaging times for the ammonia and hydrogen sulfide analyzers respectively. Adsorption of ammonia onto the walls of the chamber was found to negligibly influence the concentration after 30 minutes for concentrations above 2.5 ppm at 25°C.

Future Research

The flexibility of the measurement system lends itself to be used in many future areas of research in the areas of gaseous emissions. The system could be reprogrammed for ambient sampling or used for sampling with a wind tunnel. Future research will almost definitely play an important role in selecting BMPs for animal feeding operations.

Although flux chambers have been used for over 20 years, many of their key operation parameters are unknown. Additionally, researchers have misused the

technology as a result of not understanding the operation of a flux chamber. Researchers not using flux chambers often ask:

1. How are flowrates chosen?
2. How does the humidity and temperature affect emissions?
3. How does light effect the emission?
4. What modifications does the chamber exhibit on the emissions rate?
5. What is the effect of condensation in lines?
6. Is the chamber well mixed?

CAAQES must be able to answer these questions before flux chambers can effectively be used to evaluate emission factors for AFOs.

One key component of the sampling system could be improved to reduce analysis time for data. Data is currently logged in three locations for each sample. A wireless communication system could provide a reduction in analysis. However, the wireless communications provides additional complexity to an already multifaceted system.

Additional work with adsorption kinetics is recommended. Studies could be performed to find the adsorption kinetics on polymer tubing. Additional work could be performed to determine individual kinetics equations for stainless steel and acrylic. This will improve the estimates given by the analysis performed.

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APPENDIX A

The program structure for the enclosures is presented in this appendix. Descriptions of each program and subprogram are given. Figure A.1 shows the LabVIEW program structure. Specifics about the setup are provided in Tables A.1 and A.2.

LabVIEW Program Structure

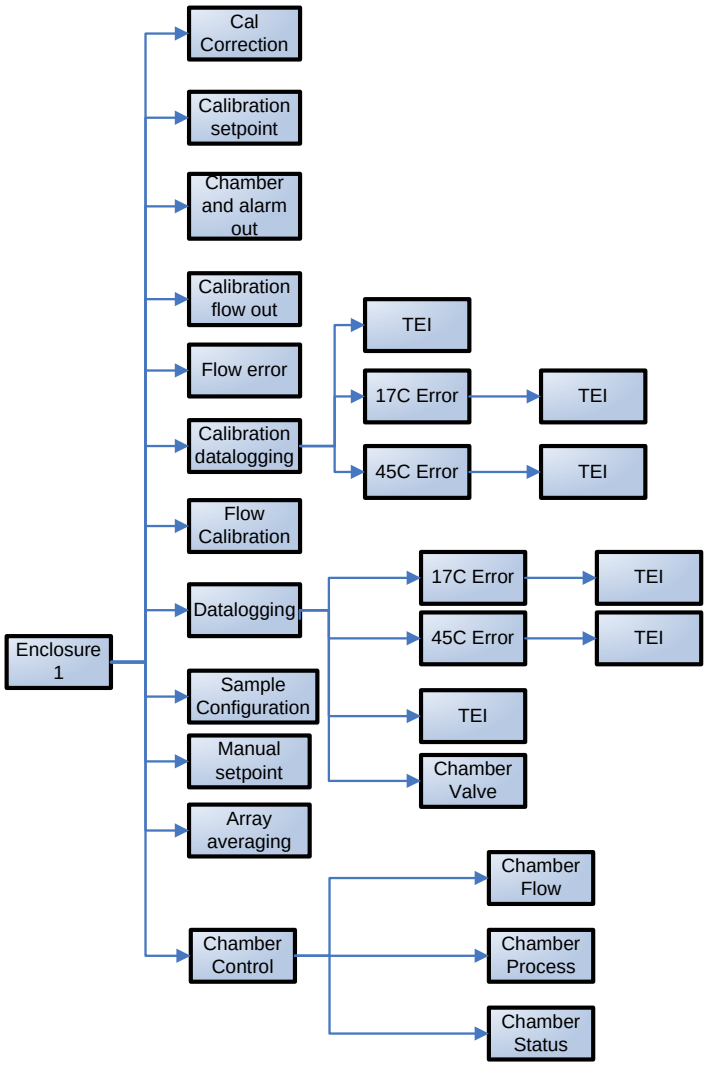

Figure A.1. LabVIEW program structure showing relationship of programs and subprograms.

FieldPoint module channel reference

Table A.1. Details about the digital output FieldPoint modules referring to the valve references of figure 5.5. The index value is the index of the array used in LabVIEW.

Ref	index	FP channel	Module
sv1	0	0	DO
sv2	1	1	
sv3	2	2	
sv4	3	3	
sv5	4	4	
sv6	5	5	
sv7	6	6	
sv8, sv16	7	7	
sv9	8	8	
sv10	9	9	
sv11	10	10	
sv12	11	11	
sv13	12	12	
sv14	13	13	
sv15	14	14	
sv17	15	15	
sv18	16	0	DO
sv19	17	1	
sv20	18	2	
sv21	19	3	
sv22	20	4	
sv23	21	5	
sv24	22	6	
sv25	23	7	
sv26	24	8	
sv27	25	9	
sv28	26	10	
ch1	27	11	
ch2	28	12	
ch3	29	13	
grn pl	30	14	
alarm	31	15	

Table A.2. Details about the digital input and analog FieldPoint modules. The index value is the index of the array used in LabVIEW.

Ref	index	FP channel	Module
CH1 on	0	0	DI
CH1rdy	1	1	
CH2 on	2	2	
CH2 rdy	3	3	
CH3 on	4	4	
CH3 rdy	5	5	
	6	6	
	7	7	
MFM1	0	0	AI
BP	1	1	
MFM2	2	2	
MFC0	3	3	
MFC1	4	4	
MFC2	5	5	
MFC3	6	6	
MFC4	7	7	
MFC0	0	0	AO
MFC1	1	1	
MFC2	2	2	
MFC3	3	3	
MFC4	4	4	
	5	5	
	6	6	
	7	7	

LabVIEW Program Descriptions

Chamber Process

Filename: *chamberprocess.vi*

This VI updates the chamber process state array.

Rows for process state array are as follows as shown also in figure 5.5:
0. Flush
1. Sample
2. Ready
3. MFC1
4. MFC2

The column indices indicate the chamber index.

"Chamber process" input is the input array.
"Chamber" input controls the ready mode of the chamber.
"Chamber process out" is the appended array after each of the commands is completed.
"Time stamp" is the time stamp when the chamber enters flush mode.
"Flush end time" is the elapsed time during flush in seconds. The default value is 1800 seconds (30 minutes).
"Sample end time" is the elapsed time to obtain a sample in seconds. The deault value is 3600 seconds (60 minutes).

Chamber and alarm out

Filename: *chamber and alarm out.vi*

This VI inputs the chamber status (chamber active) and updates the FieldPoint digital output array (valve state array) for the pilot light in the chamber switches. If an error is activated, the stack light on the enclosure changes from green to flashing red.

Manual Setpoint

Filename: *manual setpoint.vi*

This VI manually sets the flush end time to 1800 seconds and sample end time to 3600 seconds. The flow rates are set at 7 L/min. This VI may be changes to suit future needs.

TEI communications

Filename: *TEIcomm.vi*

This program sends a command to a specific Thermo C series instrument as set by the instrument id input. The program then reads a response from the C series instrument and makes the response available for parsing. The serial port for which the particular C series instrument is connected may optionally be specified by an input. If connected through FieldPoint modules, this VI must reside in the program structure of the FieldPoint and not the host computer.

The instrument ID is specified in the Instrument controls menu of the C series instrument.

The program adds a carriage return after the last character of the command automatically.

Chamber Valve

Filename: *chambervalve.vi*

This VI updates the valve state array for a given chamber process state array and backflow control.

Information for the chamber process state array is given in the chamber process VI documentation and Figure 5.5.

Valve state indices are numbered from 0-22 for valve numbers 1-23
"Valve state in" is the current state
"Valve sate out" is the new state
"Backflow" determines whether backflow is required. Backflow opens valve S8 (figure 5.4).

Chamber Status

Filename: *chamberstatus.vi*

This VI interprets the digital input data from the FieldPoint module. It contains functions for toggling the chamber status (determining whether the chamber is on or off) when used with momentary switches and interpreting the ready pushbutton data. The chamber ready out is the status of the pushbutton. The pushbuttons will only work if the chamber status bit is high.

17C error

Filename: *17error.vi*

This program parses the flag status code located on page B-23 of the 17C manual (Thermo, 2002a). The default no error code is "DC000000". The no error code assumes the:

1. Ozonator is on
2. PMT is on
3. analyzer is in remote mode
4. temperature compensation is on
5. pressure compensation is on
6. auto measurement mode
7. ppb measurement units
8. sample gas mode
9. no alarms

The program corrects for analyzer modes and reports errors to a parent vi. The VI assumes that the instrument number is 17.

The following error codes apply for the 17C with descriptions:

5001 17C In service mode
5002 17C Sample/ozone flow alarm
5003 17C Pressure high
5004 17C Pressure low
5005 17C NH_3 converter temperature high
5006 17C NH_3 converter temperature low
5007 17C NO_2 converter temperature high
5008 17C NO_2 converter temperature high
5009 17C PMT temperature high
5010 17C PMT temperature low
5011 17C Capillary temperature high
5012 17C Capillary temperature low
5013 17C Reaction chamber temperature high
5014 17C Reaction chamber temperature low
5015 17C Internal temperature high
5016 17C Internal temperature low

45C error

Filename: *45error.vi*

This program parses the flag status code located on page B-19 of the 43C manual (Thermo, 1996). The default no error code is "5C000000". (Note: the 43C is operationally identical to the 45C)

The no error code assumes the:

1. Test LED is off
2. Flash lamp is on
3. Analyzer is in remote mode
4. Temperature compensation is on
5. Pressure compensation is on
6. Ppb measurement units
7. Sample gas mode
8. No alarms

The program corrects for analyzer modes and reports errors to a parent vi. The VI assumes that the instrument number is 45.

The following error codes apply for the 45C with descriptions:

5020 45C/450C In service mode
5021 45C Concentration high
5022 45C/450C Flow high
5023 45C/450C Flow low
5024 45C/450C Pressure high
5025 45C/450C Pressure low
5026 45C/450C Lamp voltage high
5027 45C/450C Lamp voltage low
5028 45C/450C Lamp intensity high
5029 45C/450C Lamp intensity low
5030 45C/450C Reaction chamber temperature high
5031 45C/450C Reaction chamber temperature low
5032 45C/450C Internal temperature high
5033 45C/450C Internal temperature low

450C error

Filename: *450error.vi*

This program parses the flag status code located on page B-18 of the 450C revised manual (Thermo, 2002b). The default no error code is "4C000000". (Note: early versions of the manual contained the 17C flag status code)

The no error code assumes the:

1. Test LED is off
2. Flash lamp is on
3. Analyzer is in remote mode
4. Temperature compensation is on
5. Pressure compensation is on
6. Auto measurement mode
7. Ppb measurement units
8. Sample gas mode
9. No alarms

The program corrects for analyzer modes and reports errors to a parent vi. The VI assumes that the instrument number is 46.

The following error codes apply for the 45C with descriptions:

5020 45C/450C In service mode
5021 45C Concentration high
5022 45C/450C Flow high
5023 45C/450C Flow low
5024 45C/450C Pressure high
5025 45C/450C Pressure low
5026 45C/450C Lamp voltage high
5027 45C/450C Lamp voltage low
5028 45C/450C Lamp intensity high
5029 45C/450C Lamp intensity low
5030 45C/450C Reaction chamber temperature high
5031 45C/450C Reaction chamber temperature low
5032 45C/450C Internal temperature high
5033 45C/450C Internal temperature low
5034 450C SO_2 concentration high
5035 450C H_2S concentration high
5036 450C cS concentration high
5037 450C Converter temp high
5038 450C Converter temp low

Chamber Flow

Filename: *chamberflow.vi*

This VI writes the flowcontroller array for FC1 and FC2 given an input of the chamber process array.

The chamber process state array is given in figure 5.5 and details given in the chamber process VI documentation. The flow controllers are wired to channel 1 and channel 2 of the FieldPoint module.

"FC in" is the flowcontroller array in
"FC out" is the appended flowcontroller array
"Chamber process" is the chamber process array
"FC setpoint" is the voltage setpoint for each MFC

Calibration correction

Filename: *Cal Correction.vi*

This VI corrects the zero flow and calgas flow for standard conditions (SI units for air pollution). The standard conditions for the flowmeters are defined as 1atm and 21.1°C (70°F). Standard conditions in air pollution are defined as 1 atm and 25°C.

The gas flows and concentrations are output as an array containing zero flow, calgas flow, total flow, and concentration.

The concentration output from this VI is the calibration concentration that may be input into the analyzer.

Calibration Setpoint

Filename: *Calibration setpoint.vi*

This VI sets the output voltage for the flow controllers used in calibration and controls the solenoid valves used for calibration. The calibration gas input is an array that contains the calibration gas bottle concentrations. The concal input array contains the calibration gas, calibration concentration, and total flow. This VI has two modes of operation. In automatic mode, each gas is input into separate ports (S24-S28). In manual mode, only S24 is used for calibration. The calgas input array assumes a high and low concentration for each gas is used. In the main program, the input is in the form of a comma delimited file with the cylinder concentrations.

Calibration flow out

Filename: *Calibration flow out.vi*

This VI inputs the AI data from the flowmeters and outputs the flow of the flowmeters. The calibration data from each flowmeter must be input in an array. A file containing the calibration data is read from the enclosure VI. If the input flow of the sample is not between 1.5 L/min and 2.5 L/min, an error is set. The following errors are possible:

5050 Sample flow to analyzer high
5051 Sample flow to analyzer low

Flow error

Filename: *flowerror.vi*

This VI checks the ranges of flowmeters and flow controllers. If the flowmeters and flow controllers are out of range an error occurs. An error occurs if the flowcontroller is 0.1 L/min from setpoint. An error occurs from a flow flowmeter if the flowmeter is outside the range of 1.7 L/min to 5 L/min

The following error codes are supported by this VI.

5055 Flowmeter 1 out of range
5056 Flowmeter 2 out of range
5057 Flowcontroller 1 out of range
5058 Flowcontroller 2 out of range

Calibration datalogging

Filename: *Cal datalogging.vi*

This VI is used to log calibration data. It reads data from a Thermo 17C, Thermo 45C and flowmeters. The VI saves the data with a timestamp in comma delimited form to dataenc1cal.txt for further analysis.

Flow Calibration

Filename: *flowcal.vi*

This VI is used with the calibration data from flowmeters to correct voltage output from the flowcontrollers and flowmeters with an output of flow. Data is typically read from a file placed in the main folder.

Datalogging

Filename: *dataloggingb.vi*
Filename: *dataloggingb2.vi*

This VI is used to log data. It reads data from a Thermo 17C, Thermo 45C/450C, and flowmeters. Data is parsed from the C series analyzers and placed in comma delimited form to dataenc1.txt for further analysis.

Chamber Control

Filename: *chambercontrol.vi*

This VI controls chamber sampling. This control is designed according to figure 5.5. Chamber in and Chamber out should be wired to shift registers of a while loop. Chamber out additionaly may be wired to provide information such as:

valve state- output array for valves (length=32) used as inputs to two DO-401 modules
FC- flow controller input (length=8)
Chamber status- cluster indicating whether chamber is online
Time stamp-start timestamp for chambers
Chamber process- process array (see documentation on chamberprocess.vi)

Control cluster should be wired as follows:
Digital input status- wired to output of DI-330 module
Backflow- creates a control such that one can backflush inlet lines
Flush end time & sample end time- wire to constants or other VI's to control end times
FC setpoint-wire to constant or other VI to control FC setpoint

Sample Configuration

Filename: *sampleconfig.vi*

This VI builds a unique sample configuration number used to identify samples. The identification number is as follows:

[Source]_ [mmddyyhhMM]_[chamber number]_mfc[#]_enc[id]

Array averaging

Filename: *movingaveragearray.vi*

This VI averages the flow rates and outputs the averages in an array.

Enclosure 1

Filename: *enclosure1.vi*

This VI is a main VI used to control functions of enclosure 1. It manages all inputs and outputs of the system. The VI logs data, has calibration functions, and manages the multiplexer.

Input files

Files are input to the FieldPoint with the following configuration.

calgas.txt

This file contains the concentrations of the calibration gases in the following structure

0,[NO (H)], [NO (L)], [NO_2 (H)], [NO_2 (L)],[NH_3 (H)], [NH_3 (L)],[SO_2 (H)],[SO_2 (L)],[H_2S (H)], [H_2S (L)]

where, the brackets indicate concentrations of the gas. Two concentrations are allowed for each gas.

concal.txt

This file contains the calibration information from the touch screen. The information is formatted in the following manner:

[calibration gas (0-10)],[calibration concentration{ppb}],[total flow{L/min}]

rlmode.txt

This file contains information about the remote/local mode. The file contains either "remote" or "local" in it. This file is programmed internally from the touchscreen. In local mode, the touchscreen provides the input. In remote mode, a computer may be attached through a wireless connection to provide the overall functionality.

sa.txt

This file contains text that identifies the sample location. Text from this file is input into the unique sample identification number.

sampleno2.txt

This file contains an 8 digit number that is used to check the last record saved. The number is processed from the dataenc1.txt file when a record is saved to the compact flash.

scmode.txt

This file contains information about the sampling/calibration mode. The file contains either "sample" or "calibrate" in it. This file is programmed internally from the touchscreen.

Output files

The enclosure1 VI outputs the following files from the FieldPoint module.

armenc1.txt

This file contains information used by the touchscreen in sampling mode.

armenc1cal.txt

This file contains information used by the touchscreen in calibration mode.

dataenc1.txt

This file contains records from the sampling mode that are saved to the compact flash for further analysis.

dataenc1cal.txt

This file contains records from the calibration mode that are saved to the compact flash for further analysis.

sampleno2.txt

This file contains an 8 digit number that is used to retain the last record number. The number is processed from the dataenc1.txt file.

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